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THE TECHNOLOGY OF THE FISCHER-TROPSCH PROCESS

THE TECHNOLOGY OF THE FISCHER-TROPSCH PROCESS

(Published in the U.S.A. under the title "Synthetic Petroleum from the Synthine Process.")

by

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FOREWORD

Along with the constantly accelerating growth of the art of catalysis has come the industrial development of the chemistry of carbon monoxide. The synthesis of normal- and iso-paraffins and C_4 to C_{20} normal- and branched-chain alcohols has been added to such earlier processes as the water-gas shift and the synthesis of oxygenated compounds, such as methanol and higher alcohols. Moreover, research at very high pressures with special catalysts indicates the possibility that polyhydric alcohols may be one of the prizes of this field of endeavour.

This book on synthetic petroleum is like an incomplete moving picture of the erection of a large building or cathedral, with faithfully recorded sound effects. The basic foundation is visible, along with a few parts of the superstructure. The chatter of workmen and the sound of hammer, saw, and other hand tools mingle with the constant drumming and buzzing of power tools. Without access to the architects' final plans, however, one can only guess as to the details of the remainder of the structure. Similarly, the foundation of the Fischer-Tropsch-Pichler (Synthine) process is far from complete. Much is known empirically, but the basic chemical and physical factors of the synthesis are even now being carefully explored, using all of the powerful, recently developed physical-chemical tools, such as isotopic tracer- and magneto-chemistry.

The ingenious (albeit largely intuitive) process development in Germany and the United States has resulted in the production of aliphatic hydrocarbons and alcohols at costs that already are almost competitive with existing processes based on natural petroleum. This development work, however, has emphasized the need for rational (mathematical rather than empirical) design of pilot plants. Such design must have the results of carefully planned laboratory research for its basis.

It is to be hoped that the record presented in this book will stimulate such research and rational pilot-plant design. In any event, this text will serve as a timely and valuable reference.

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PREFACE

IN THE life of any chemical process of wide applicability and diverse technology, there comes a time when individual articles and patents, literature reviews, and even booklets or sections of books become too limited in size to describe it adequately. Such is the case with the Fischer-Tropsch (Synthine) process, and it is for this reason that the authors of this book have undertaken the preparation of what will probably be the first of a number of books which this process seems likely to inspire.

In the course of the authors' work in the field of petroleum refining, they have had occasions to prepare several searches and surveys of the literature and patents on the Fischer-Tropsch process, covering the subject in as exhaustive a fashion as facilities permitted. Early in 1946, noting the need for a comprehensive review of the pertinent data, they prepared a series of four articles on this subject for the *Petroleum Refiner*, in an attempt to correlate the more significant facts into a coherent whole and, at the same time, to present a representative bibliography for further study. Space prohibited inclusion of all of the some 3,000 related articles, books, and patents which had been identified, but more than enough were used to authenticate the information presented.

Encouraged by the response to the appearance of these articles, the authors have attempted in this book to include data omitted from the articles for want of space, recent information, and—more important—appendices which contain reference bibliographies of related patents, Government reports, and supplemental material. As in the articles, the Fischer-Tropsch process is treated under the four categories into which its copious subject matter appears to fall: (1) production and purification of the synthesis gas, (2) catalytic synthesis reactions, (3) products, by-products, and derivatives, and (4) basic economics and current developments.

The status and technical details of the Fischer-Tropsch process are dealt with at such length in the book proper that little in the way of further introduction seems desirable here. It might be mentioned that the Fischer-Tropsch process offers almost unlimited possibilities for the manufacture of synthetic aliphatic chemicals and their derivatives and, either through aromatization or in conjunction with coal hydrogenation (which yields largely aromatics), makes possible the synthesis of almost any organic compound from "coal, water, and air." In regard to its possibilities as a process for the synthesis of

"petroleum", it is certainly more than interesting to note the general belief that certain variations of the Fischer-Tropsch process using natural gas as raw material are competitive with petroleum at present prices and that even the eventual use of coal will not add more than three or four cents per gallon to the cost or gasoline so produced.

While the bulk of natural gas reserves will undoubtedly have to be largely allocated (for economic reasons, if nothing else) to such other uses as are peculiar to its physical form, considerable quantities will certainly be available for conversion to oil for a number of years, and coal reserves are sufficient to last for 3,000 years at the present rate of consumption—to produce as much as 6 million million barrels of gasoline in the extremely unlikely case that all would be so converted.

The authors do not believe, of course, that the Fischer-Tropsch process will be the only method employed on a large scale when—at long last—the supply of petroleum runs low. Shale oil, oil from tar sands, and possibly even coal hydrogenation products and agricultural derivatives will all play their part. Nevertheless, there appears to be fairly general agreement at present that the Fischer-Tropsch process—the catalytic hydrogenation of carbon monoxide—is the most economic of all the synthetic liquid fuel processes based upon that ultimate raw material coal, and that its use in America should, in the next few decades, greatly exceed its nationalistic and therefore economically inept applications in Germany in the two decades which have followed its discovery.

The Fischer-Tropsch process is of vital significance to the petroleum industry, the coal industry, the natural and manufactured gas industries, and the chemical industry, and through these to the millions of users of liquid and gaseous fuels and chemical derivatives —the American nation as a whole. The authors hope that this book will in some manner contribute to its understanding and effective use.

The authors wish to express their appreciation to Mr Grady Triplett, editor of the *Petroleum Refiner*, for his permission to make liberal use of the material appearing in the four articles which they recently prepared for that journal, and to Mr Eugene Ayres, chief chemist, and Dr Paul D. Foote, executive vice-president of the Gulf Research and Development Company, for their interest in this endeavour and their permission to make use of search material. Thanks are also extended to Dr Gerald A. Rosselot and Dr Paul Weber, director and assistant director of the State Engineering Experiment Station, Georgia School of Technology, for their active interest in this book, and to Dr H. H. Storch, chief of the Research

and Development Division of the Office of Synthetic Liquid Fuels, for his kindness in writing the Foreword.

Valuable assistance in the preparation of the Government report appendix was obtained from Mrs Dorothy Gordon, chief of reference services in the Bibliography and Reference Division of the Office of Technical Services, United States Department of Commerce and from Dr L. L. Newman, chief of the Foreign Synthetic Liquid Fuels Division, Bureau of Mines, United States Department of the Interior. Numerous illustrations were kindly provided by Dr W. C. Schroeder, chief of the Office of Synthetic Liquid Fuels (Bureau of Mines); Dr H. H. Storch, chief of the Research and Development Division of the Office of Synthetic Liquid Fuels; Dr A. R. Powell, associate director of research of the Koppers Company, Inc.; and Mr R. C. Alden, director of research of the Phillips Petroleum Company.

Acknowledgement for varied assistance is also gratefully made to Dr W. A. Horne, Mrs Nancy Marie Lane, Mrs J. C. Loeb, Mrs Doris Morris, Mrs Carolyn L. Weil, and Mr Sidney E. Winn.

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Part I

SYNTHESIS GAS

Chapter 1

INTRODUCTION

PETROLEUM is the life blood of the United States, both in peace and in war. Automobiles, trucks, tractors, airplanes, and ships depend upon it for motive power, and it is increasingly used to supply energy and heat to homes and industries. Its use and importance in World War II were far too great and too recent to require description here.

The peacetime utility and wartime indispensability of petroleum have induced economists, business men, scientists, and the general public alike to view with decided interest all of the facts and controversies over the extent of future supplies. No decision in this argument has yet been reached, nor is it fitting here to attempt to derive one. What does seem clear, however, is that: (1) domestic peacetime petroleum demand will continue to rise; (2) domestic costs of exploration and discovery will continue to increase; (3) any near-future war will require vast quantities of petroleum both in the field and at home, where shortages nearly caused a breakdown during the recent conflict; (4) nuclear (atomic) energy will probably first be utilized to provide power and heat on a large scale for industries and communities, its use to motivate ships, trains, and giant aircraft coming only after a number of years, and perhaps never for automobiles as we know them;[4] and (5) solid fuels, unforeseen developments aside, will never be as convenient for certain uses as are the products of petroleum.

Many economic factors will continue to play their part in the future scene. Rising domestic petroleum prices in America may cause some shifts to other fuels, unless the price increase is checked by a flood of foreign oil. Users of petroleum products will be provided with more efficient equipment. Conservation pressure plus higher prices may cause the widespread use of destructive hydrogenation of heavy residues and low-grade crudes, thus lessening the required ratio of crude oil to gasoline.

Several petroleum economists have forecast petroleum demands in the United States for the next decade, or even longer, using premises which are sound and logical as far as past experience can foretell. All of these economists agree that these demands will call for such vast quantities of oil that production will have to be materially increased or imports expanded. Considering these circumstances,

there is little wonder that much attention is being given to the subject of petroleum substitutes. A great part of this interest is being directed toward the use of the Fischer-Tropsch process—the production of synthetic petroleum products by the catalytic hydrogenation of carbon monoxide.

The Fischer-Tropsch Process

This process is of particular interest because its raw materials, hydrogen and carbon monoxide, can be obtained from many substances in many ways. In particular, they may readily be derived from natural gas or coal, the first material offering decided economic advantages in America and the second providing assurance that reserves are almost inexhaustible.

Gasoline and other "petroleum" products have never been produced commercially by the Fischer-Tropsch process in America, but plans for the first full-scale plant, using natural gas, have virtually been completed,[1, 3, 7, 9] and the plant may even be in operation before 1949. In Europe, however, the process has been in actual use for over a decade, and it has been said that only intercompany rivalry prevented it from playing as important a role in Germany during the recent war as did the hydrogenation of coal.[2]

History

The fact that a hydrocarbon (methane) could be catalytically produced from carbon monoxide and hydrogen was early observed by Sabatier, and in 1913 the Badische Anilin und Soda Fabrik revealed that mixtures of higher hydrocarbons and oxygenated compounds could be catalytically produced from a similar mixture under high pressures.[12] Ten years later, Franz Fischer and Hans Tropsch, who had noted similar results in work with an alkali-iron catalyst at 750-840° F. and 1470-2200 pounds per square inch pressure,[5] observed that increasing yields of hydrocarbons were obtained as reaction pressures were lowered and that these compounds definitely predominated at pressures lower than seven atmospheres. More active catalysts were required to increase yields, however, since these fell rapidly with the decrease in pressure, and it was not until 1925-26 that the discovery of suitable catalysts for a process operated at atmospheric pressure and 482-572° F. was announced.[6, 13]

The chemical mechanism of the Fischer-Tropsch process has been the subject for much debate, some of which will be given in detail in Part II. According to one of the current theories, [8, 11] the catalyst must serve a dual function—hydrogenation and polymerization;

other functions, such as isomerization and perhaps even cracking, may be required of future optimum catalysts.

The process was put into commercial operation in Germany in 1936, and by 1940, the annual production showed a tenfold increase. An up-to-date, general account of the process for the production of oil from coal has been given by Hall.[14] France, Japan, and Manchukuo erected plants, and the process received intensive study in England and America. One phase of the present $60,000,000 synthetic liquid fuels programme of the U.S. Bureau of Mines deals with the Fischer-Tropsch process as an outgrowth of some of the Bureau's early research, and many American petroleum and coal companies have engaged in similar intensive studies.

Nomenclature

It seems timely here to dispel some of the confusion which the use of different terms for the process appears to have engendered. The term, "Synthine", is one which has gained much favour in the United States in recent years, primarily because it is a contraction of the words "*synth*etic" and "gaso*line*." It is true that such a coined word could be applied, if desired, to any synthesized gasoline, and that other "petroleum" products are also produced by the reaction. However, the term has the added advantage of being the Anglicized form of the German "Synthin," a contraction of "*synth*etisches Benz*in*," a term which the Germans have long applied to the process and its chief product.

The mixture of hydrocarbons and oxygenated compounds obtained by Fischer and Tropsch in their early work was given the name "Synthol," and this term is currently being applied to a version of the process developed in the United States by one engineering concern.[10] This use may be (1) a carry-over from early days of co-operation with German interests, or (2) the process used may actually resemble the original "Synthol" method and produce oxygenated compounds in addition to hydrocarbons. The second premise is rendered plausible by the fact that press releases by this company have discussed oxygenated compounds as by-products. No detailed technical information has yet been published. In any case, the term "Synthol" is far from being sufficiently representative for general application.

Considerable use has been made of the term "Fischer-Tropsch" process, for obvious reasons. This is perhaps fitting, since the basic contributions of these men are beyond refutation. However, the variations of their process are now so numerous that many companies do not particularly care to designate their methods by this term.

Certain other German terms are not likely to dominate the domestic scene but are of importance because of their frequent occurrence in the literature. In Germany, where the process depends chiefly upon coal for the preparation of the synthesis gas, it was fairly logical to give the products the coined name, "Kogasin," derived from the German words for coal, gas, and gasoline (*Ko*hle-*Gas*-Benz*in*). "Kogasin I" was the name given to the naphtha fraction (boiling from 86-392° F.), while the term "Kogasin II" was used for the heavier hydrocarbon products (gas oils, Diesel fuels, etc.). These terms would certainly be inappropriate in the United States, where natural gas will almost certainly prove to be the preferred raw material for the process.

It seems likely, then, that the term "Synthine", possibly uncapitalized, will become increasingly associated with the many variations of the hydrogenation of carbon monoxide to yield petroleum-like products. The word may be also applied to the products of the synthesis—Synthine gasoline, Synthine gas oil, etc. —which products, in turn, may be generally classed as "Synthinates." "Synthine" appears to be a much less unwieldly term for the process than the awkward (and not sufficiently inclusive) title "the indirect hydrogenation of coal."

(*Note.* Outside the United States, the term "Fischer-Tropsch" is still preferred to describe this process, and has accordingly been used in the English edition of this book.)

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Chapter 2

SYNTHESIS GAS FROM COAL IN SURFACE PRODUCERS

DEPENDING upon the catalyst employed in the synthesis reaction, the conditions of operation, and the products desired, the optimum ratio of hydrogen to carbon monoxide in the synthesis gas used in the Synthine process ranges from about 2 to 1 to less than 1 to 1. The standard synthesis with cobalt catalyst usually requires the former ratio, while the so-called "iso-synthesis," carried out over catalysts containing zinc oxide, aluminium trioxide, and thoria, uses a ratio of about 1 to 1.2.[21, 22] Although the direct hydrogenation of coal requires hydrogen of at least 92 per cent purity, the Fischer-Tropsch process is reported to operate satisfactorily on gases containing as much as 10-12 per cent of inerts (carbon dioxide and nitrogen).[44]

Theoretically at least, any carbonaceous material which can be decomposed to hydrogen and carbon monoxide can be used in the production of synthesis gas, but as mentioned, only coal and natural gas have thus far appeared of commercial interest. European operations have necessarily utilized coal because of the insufficient quantity of natural gas available on the Continent. It is generally believed, however, that synthesis gas can be prepared more economically from natural gas (at present price levels) than from coal.

The more important, commercially practical methods for producing hydrogen- and carbon monoxide-rich gas mixtures from coal include the following:

(1) Manufacture of water gas from coke in standard water-gas sets;
(2) Manufacture of water gas from low-volatile coal in more or less standard equipment;
(3) Manufacture of water gas from coal or coke using oxygen in the steam blast; e.g. in Winkler and Lurgi equipment; and
(4) Conversion of coke-oven gas with steam, either catalytically or noncatalytically.

Since the theoretically ideal water-gas reaction may be written: $C + H_2O \rightarrow CO + H_2$, approximately equal amounts of hydrogen and carbon monoxide might therefore be expected from practical

utilization of the reaction. Typical compositions of gases actually obtained by the processes mentioned above are given in Table I.

FIG. 1. *Becker underjet by-product coke ovens, at Kearny, N.J. The conventional Fischer-Tropsch operations are based on coke as the raw material.* (Courtesy of Koppers Company, Inc.)

In order to convert the gases from any of these processes into synthesis gas, it is necessary to adjust the hydrogen-carbon monoxide ratio to the desired value, usually about 2 to 1. In the case of water gas, this may be accomplished by the well-known water-gas-shift reaction: $CO + H_2O \rightarrow CO_2 + H_2$. A catalyst is required in this reaction, the usual one consisting of ferric oxide promoted by the oxides of chromium, calcium, and magnesium.[9, 10] Partially reduced cobalt oxide;[50] cobalt catalysts containing about 38 per

cent of copper;[45] magnesia and zinc oxide promoted with potassium oxide;[31] catalysts composed of active carbon and magnesia;[39] and nickel catalysts promoted with a variety of non-reducible oxides preferably magnesia,[12, 48] have all been proposed as shift catalysts. The carbon dioxide formed in the shift reaction may be removed by compressing the gas and scrubbing it with water or by reacting it with ethanolamines, which are subsequently regenerated.[41]

TABLE I

Typical Compositions of Gases Produced from Coal or Coke by Various Methods.[41, 44]

Charge		*Low-*			*Non-*	
Method	*Coke*	*Volatile*	*Coke*	*Coke*	*coking Coal*	*Coal*
Equipment	*Water-Gas*	*Coal*	*Water-Gas*	*Water-Gas*	*Water-Gas*	*Coke Oven*
	Standard	*Water-Gas*	*Winkler*	*Winkler*	*Lurgi*	*Coke Oven*
		Standard	(O_2+H_2O)	($O_2+Air+H_2O$)	(O_2+H_2O)	(*Debenzol-*
Gas						*ized*)
Composition						
CO_2	5	3.8	13-20	15.2	30	3.0
CO	41	39.7	47-36	32.9	20-15	7.0
H_2	50	54.1	39-41	29.7	30-35	55.0
CH_4	0.5	0.7	0.6-0.4	1.3	15-20	27.0
N_2	3.5	1.5	0.4-0.5	20.9	2.0	6.0
C_nH_m	—	0.2	—	—	—	2.0

Coke-oven gas, while rich in hydrogen, contains relatively little carbon monoxide, considerable methane, and some unsaturated hydrocarbons, chiefly ethylene. These hydrocarbons may be converted to hydrogen and carbon monoxide by reacting the coke-oven gas either catalytically or noncatalytically with steam. Catalysts suitable for the reaction are those later specified for the production of synthesis gas by the "methane-steam" reaction. From 100 volumes of coke-oven gas of the composition given in Table I, it is said to be possible to obtain 190 volumes of converted coke-oven gas of the following composition:[41]

	per cent
CO_2	4.2
CO	16.3
H_2	75.3
CH_4	1.0
N_2	3.2

In this gas, the ratio of hydrogen to carbon monoxide is too high, in contrast to water gas in which it is too low. However, mixture of the 190 volumes of converted coke-oven gas with 250 volumes of water

gas made from coke in a standard water-gas set (composition in Table I) would yield 440 volumes of synthesis gas of the following composition:

	per cent
CO_2	4.6
CO	30.4
H_2	60.9
CH_4	0.7
N_2	3.4

"An alternative method of operation is to blow the water-gas generator with a mixture of steam and coke-oven gas (10 cubic feet of coke-oven gas per pound of steam), whereby synthesis gas is produced in one stage."[41] Blowing the generator with a mixture of steam and coke-oven gas either alternately with steam-oxygen blasts or continuously in admixture with oxygen has been claimed in several patents.[54, 55, 56]

FIG. 2. *General view toward water-gas machines of the Ruhrchemie.* (Courtesy of W. C. Schroeder, U.S. Bureau of Mines.)

Some valuable papers recording recent American work on the production of synthesis gas were presented at the 112th Meeting of the American Chemical Society.[60]

German Methods

Recently released information obtained by the Allied investigation of German synthetic gasoline plants illustrates the various methods and combinations of methods the Germans were using to produce

synthesis gas from coal.[57] This information has revealed that the majority of the commercial-scale German plants made their synthesis gas from coke by means of the water-gas reaction, followed by a catalyzed water-gas-shift to obtain the desired ratio of hydrogen to carbon monoxide. The German water-gas-shift catalyst is said to have analyzed 38.5 per cent ferric oxide, 18.2 per cent calcium oxide, 5.4 per cent chromic oxide, 5.2 per cent magnesium oxide, with minor amounts of other constituents, including 18.0 per cent water, differing little from that commonly used for the reaction.[9]

FIG. 3. *Water-gas plant for synthesis gas production. Hoesch-Benzin.* (Courtesy of W. C. Schroeder, U.S. Bureau of Mines.)

The cracking of coke-oven gas was utilized in a number of the German plants in order to produce a hydrogen-rich gas for admixture with water gas, thus minimizing the amount of water gas subjected to the shift reaction. As an example of such a combination of synthesis gas processes, the synthetic gasoline plant of Steinkohlen-Bergwerk Rheinpreussen at Moers-Meerbeck (near Homburg), Germany, manufactured about 41,000,000 cubic feet of water gas daily in eleven standard Koppers [34] water-gas generators. About 18 per cent of the water gas (about 7,400,000 cubic feet per day) was then passed through a shift apparatus with normal shift catalyst to increase its hydrogen content. Approximately 353,000 cubic feet per hour (about 8,500,000 cubic feet per 24-hour day) of coke-oven gas were "cracked" noncatalytically with steam at about 2200° F. in six Cowper stoves to bring the hydrogen-carbon monoxide ratio up to 2 : 1, which was the desired ratio at that plant.[10]

Several less conventional methods of making synthesis gas were in operation in some German synthetic gasoline plants. At Wanne-Eickel, the Krupp-Lurgi process for the manufacture of low-temperature coke was employed to make a coke which, when used in water-gas sets, gave blue water gas with a hydrogen-carbon monoxide ratio of 1.35 to 1, this ratio being nearer that required for synthesis gas than that of water gas manufactured from high-temperature coke.[9, 23]

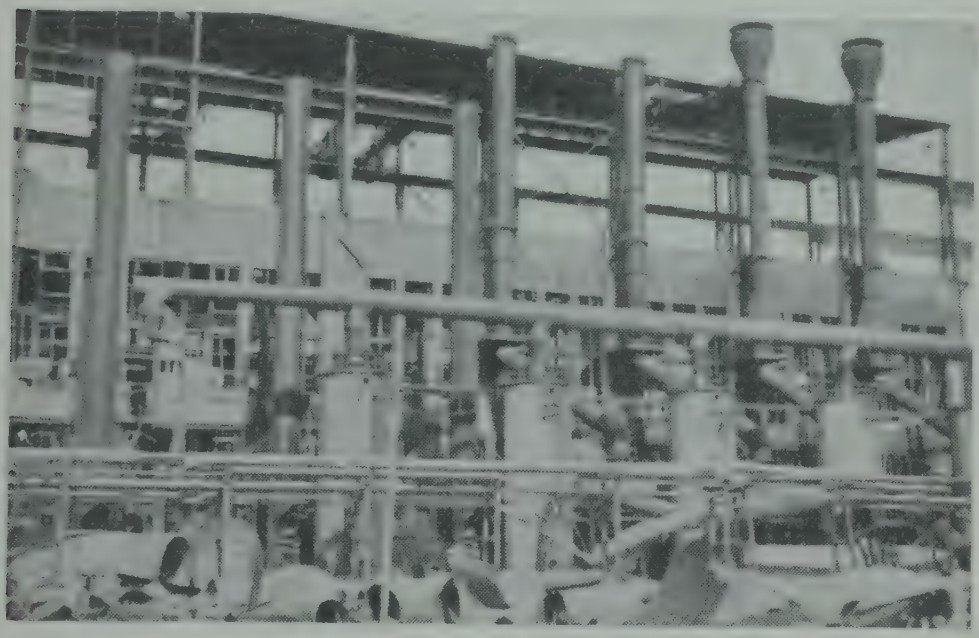

FIG. 4. *Pintsch-Hillebrand gas washer, with holders in front. Ruhrchemie unit.* (Courtesy of W. C. Schroeder, U.S. Bureau of Mines.)

The Pintsch-Hillebrand process for the complete gasification of brown coal or other noncoking coals to either synthesis gas or hydrogen was reported to provide the necessary heat for the water-gas reaction by passing steam and previously-formed water gas through regenerators heated in alternate cycles by combustion of producer gas.[9, 33]

The Schmalfeldt-Wintershall process[58, 59] for the manufacture of synthesis gas from noncoking coal was said to have been under large-scale development when the war began. This process is said to be indifferent to the moisture and ash content of the charge, and thus particularly suited for use on run-of-mine coals.[21] In the original process, very finely-pulverized coal was first dried in a stream of hot recirculating gas, removed in a cyclone separator, and fed into a generator with a hot stream of recirculating gas containing sufficient make-up steam for complete gasification, a portion of the recycle

stream being continuously withdrawn as synthesis gas. Interrogation of German technical men is reported to have revealed that a number of difficulties were encountered in commercial operation of the process, however.[37] Plans for the revision of a large installation built by Wintershall A.G. at Luetzkendorf in central Germany were revealed in a document found at Leuna in I. G. Farbenindustrie's possession.[9] Lack of gas-producing capacity was said to be one of the shortcomings of the process. According to interrogated Germans, increased capacity was obtained by installing a new type of rotating-grate generator and adding oxygen in relatively small amounts to increase the heat available for gasification. Since the gas from this process contained only 76 per cent hydrogen plus carbon monoxide, the plant would have required 4,000,000 cubic feet per hour of synthesis gas in order to produce 82,500 short tons of Fischer-Tropsch products per year. Four generators, plus one spare, were needed to produce this quantity of gas. About 4,325,000 cubic feet per hour of producer gas were required for heating purposes, and about 49,500 cubic feet per hour of oxygen for addition to the generator. Approximately 50 pounds of brown coal (dry basis) were required to make 1000 cubic feet of synthesis gas by this method.[9]

The raw material requirements of the various generators vary according to the type and efficiency of the installation. The standard-type Koppers generators used in the Steinkohlen-Bergwerk plant at Moers-Meerbeck charged about 981 metric tons per day of coke containing 82.6 per cent carbon and volatile matter, 8.2 per cent water, and 9.2 per cent ash in order to obtain a daily output of 1,146,070 cubic metres of water gas.[33] In English units this is approximately 53.5 pounds of coke per 1000 cubic feet of water gas.

Winkler generators [26] charge lignite, coal, or semicoke reduced to a particle size of about one-fourth of an inch. Oxygen and steam; or air, oxygen, and steam are added in such a way that the fuel is kept in a constant state of agitation. The composition of Winkler water gas from coke both with and without air in the oxygen-steam stream is given in Table I. Raw material consumption per 1000 cubic feet of gas is as follows:[44]

	Oxygen + Steam	*Oxygen + Air + Steam*
Coke, pounds	40.9	33.0
Air, cubic feet	—	242
Oxygen (98%), cubic feet	284	179
Water, pounds	19	13.2

Winkler process plants in actual German use were said to be superior to Schmalfeldt process plants, although a properly-designed plant using the latter method was thought to be economically superior.[37]

The Didier gas generator,[46] which charges ¼- to 1-inch briquets of bituminous coal or lignite, is a combination of a vertical retort and a water-gas generator, both being operated continuously. A gas suitable for use in the Fischer-Tropsch process is obtained from this apparatus by *in situ* conversion of the distillation gas which is then blended with the water gas simultaneously produced in another zone. A part of the heat requirement of the process is said to be supplied by the sensible heat in the off-gas, and the remainder by the heat of reaction of the subsequent catalytic synthesis. The thermal efficiency when using lignite briquets is claimed to be about 75 per cent.[44]

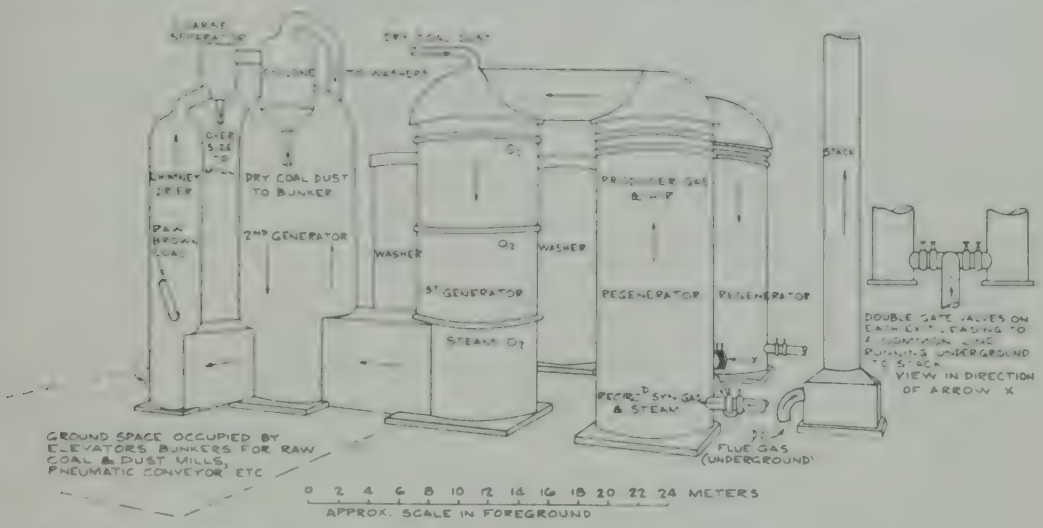
DRY COAL DUST TO BUNKER
2ND GENERATOR
WASHER
WASHER
1ST GENERATOR
REGENERATOR
REGENERATOR
STEAM
STACK
GROUND SPACE OCCUPIED BY ELEVATORS BUNKERS FOR RAW COAL & DUST MILLS, PNEUMATIC CONVEYOR ETC
FLUE GAS (UNDERGROUND)
VIEW IN DIRECTION OF ARROW X
0 2 4 6 8 10 12 14 16 18 20 22 24 METERS
APPROX. SCALE IN FOREGROUND

FIG. 5. *Schmalfeldt-Wintershall synthesis gas unit.* (*Simplified but roughly to size.*)

The Lurgi process for complete gasification of various solid fuels using steam and oxygen under pressure,[3, 15, 18, 24, 30, 35, 40, 51] the previously-mentioned Pintsch-Hillebrand process,[2, 9, 33, 42, 43] and other processes and equipment[13, 17, 27, 32, 38, 46, 52] have all been described in the literature, and the economic advantage of complete continuous gasification has also been discussed in several articles.[7, 25, 29, 49, 53] In addition to a number of other references on continuous gasification processes,[1, 5, 6, 14, 53] a review on large-scale water-gas production, including numerous details on the various processes, has been given by Thau;[47] several other articles have treated the subject at more or less length.[4, 8, 11, 19, 20, 28, 36] According to Dolch,[15, 16] the oxygen-steam processes give gas yields which are superior to those from processes in which the heat is obtained by the separate gasification of part of the fuel. He also has claimed that processes of carbonization and gasification in vertical ovens at atmospheric pressure with oxygen-steam mixtures produce a low-methane gas and require the least oxygen.

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Chapter 3

UNDERGROUND GASIFICATION OF COAL FOR SYNTHESIS GAS PRODUCTION

AS PREVIOUSLY mentioned, the higher cost of producing synthesis gas from coal renders it probable that commercial Fischer-Tropsch operations in the United States will utilize natural gas as the raw material until such time as the economic advantage is lost as a result of approaching depletion of gas reserves and the consequent higher prices brought about by competition for the lessened supply. However, the quantity of coal available for conversion to liquid fuel is vastly greater than the amount of natural gas which could be diverted to this purpose, and keen interest awaits the development of any process which can produce synthesis gas from coal at less expense than the methods now in use. The underground gasification of coal shows strong potentialities of becoming just such a process, since it gasifies the coal *in situ* and entails no costs for mining and transportation of the raw material or for elaborate gasification equipment.

Although Siemens in 1868 and Mendeléev in 1888 suggested the idea, and Betts in 1909 patented a process, there is no record of actual experimentation on underground gasification until just before the first World War, when Sir William Ramsay began investigations near Tursdale Colliery, Durham, England.[9] However, Ramsay's project was discontinued at the outbreak of war, and no appreciable work along this line appears to have been done until after 1931 when the Soviet Government decided to subsidize experiments on underground coal gasification. The Podzemgaz trust was formed in 1933, and some preliminary experimental work was done in that year. The first experimental station for the gasification of coal on an industrial scale began operation in the Donets coal field in 1937, while the first truly commercial installation went into operation late in 1940. The Third Five Year Plan (1938-42) is said to have called for construction of plants in the Donets and Moscow coal fields and in the Urals, Eastern Siberia, Central Asia, and the Far East. While the proposed scale of these operations is not completely known, it has been stated that the station at Lisichansk (in the Donets coal field) was expected to have a daily output of 20,000,000 cubic feet of gas with an average calorific value of 275 B.Th.U. per cubic foot. Two of the other proposed stations were to have daily capacities of 14,000,000 and 8,000,000 cubic feet respectively.[3]

Four different methods of underground gasification have reportedly been investigated by the Russians: (1) the "chamber" method, (2) the "stream" method, (3) the "percolation" method, and (4) the "crevice" (or "borehole-producer") method.[21] With the exception of the chamber method, which is considered obsolete, each of these processes is especially adaptable to a particular type of seam, the determining factors in the choice of the particular method usually being the seam's inclination and depth. The Russians are said to have carried out underground gasification experiments on coal seams ranging from 1-16 feet in thickness, 65-200 feet in depth, and 0°-75° in inclination.[19]

Chamber Method

The chamber method,[2, 9, 10, 11] which consisted of isolating a panel of coal from the rest of the seam by means of brickwork walls and constructing shafts on opposite sides of the panel for the air inlet and gas offtake, was the earliest method investigated by the Russians. Two variations of the method were tried, one in which the natural fissures and porosity of the coal seam were utilized for the passage of the air and gas through the chamber, and the other in which the coal in the chamber had been previously broken up. Although the chamber method was workable, it still required considerable underground labour for preparation of the chambers and was abandoned in favour of the other three processes.

Stream Method

The stream method of underground gasification involves driving a gallery lengthwise along the coal seam to connect two shafts drilled from the surface to the level of this gallery, thus forming a panel of coal with an air inlet and a gas outlet at opposite ends. A fire is started at the base of the air inlet shaft, the air blast admitted, and the gas taken off at the other shaft. The fire burns progressively upward toward the roof of the seam, and the ash, together with any of the unburned coal which may fall, collects in the space below the fire zone. Three zones of reaction are said to exist in the gallery of the stream method. In a test panel 7.5 metres long, their identity and extent were found to be as follows:[6, 17]

(1) The "combustion" zone, extending for about 2.5 metres, in which the coal burns mainly to carbon monoxide;
(2) The "recovery" zone, extending for about 3 metres, in which the carbon dioxide is reduced to carbon monoxide and considerable amounts of hydrogen appear in the gas; and

(3) The "distillation" zone, extending for about 2 metres, in which the carbon dioxide content of the gas becomes constant and the gas is enriched by carbonization of the coal face.

The coal consumption is not equal in all three of these zones, the maximum amount being consumed in the combustion zone. Therefore, the direction of the blast is periodically reversed in order to avoid unsymmetrical burning out of the panel.

Unless steam is added to the air blast, the gas from underground gasification is deficient in hydrogen as regards normal synthesis gas requirements. A regenerative variant of the stream method, in which air and steam are blown for 20- to 30-minute periods alternately in opposite directions, is said to produce a water gas of the following composition:[5]

	per cent
CO_2	15
CO	26
H_2	53
CH_4	0.7
O_2	0.5
N_2	4.8

The stream method requires a fairly small amount of underground labour, and by directional drilling, it is conceivable that the gallery as well as the shafts could be drilled from the surface, since it is by no means essential that this gallery be perfectly horizontal. Another proposed design for an underground gas generator consists simply of two shafts drilled from the surface in a V-shape, one to serve as air inlet and the other as gas outlet, the fire being built at the intersection of the shafts.[4] The stream method is particularly suited to steeply inclined seams. In horizontal or only slightly inclined seams, the access of air to the coal face becomes obstructed by ash and fallen, unconsumed coal.

Percolation Method

The percolation (or filtration) method, patented in 1909,[20] depends on the formation of shrinkage cracks and fissures in the coal when heated, so that it becomes readily permeable to gas. This method is particularly applicable to horizontal seams and requires no underground mining. In commercial practice, vertical holes are drilled into the seam in concentric rings spaced 20-40 yards apart radially. Starting-up operations consist of building fires at the bottom of the adjacent shafts, blowing air down central pipes, and collecting

he gas produced, which passes up the same shaft around the central ipe. The heat from these underground fires develops cracks and issures in the coal, so that it becomes possible for the gases in one ole to pass through the seam to the adjacent hole. As soon as this ondition is established, the gas offtake of one of the holes and the air nlet of the other are sealed, and gasification of the panel between the oles is begun. When the coal between these two holes has been asified, one of the holes is sealed off and an adjacent hole brought nto use, the panels between all of the holes eventually being gasified n succession.[19]

In one modification of the percolation method, three concentric circles of vertical holes are drilled, each circle being connected at the top by headers. Air at five atmospheres pressure is blown in at the inner circle of holes and oxygen at eight atmospheres at the outer circle, the gas produced being taken off from the middle circle.[7]

A combination of the percolation and stream methods has been suggested for use in horizontal seams where the stream method fails because of collapse of the roof. The seam to be gasified is divided into squares by vertical shafts and these shafts are connected at their lower ends by horizontal borings. The stream method is used until the horizontal borings (called "fire-drifts") become obstructed by roof falls and ash, after which gasification is continued by the percolation method, assuming that the adjacent coal has become sufficiently porous for this method.[14]

Crevice Method

In the crevice method of underground coal gasification, three parallel shafts, each of about 2 feet in diameter, are drilled from the surface into the coal seam, the centre shaft serving as the blast inlet and the shafts on either side serving as gas-offtake manifolds. The shafts are then connected by a series of holes of about 4 inches in diameter and 5 yards apart, so laid out that they are parallel to each other and intersect the shafts at right angles.

Various methods for constructing these shaft-connected holes have been employed. One method, "hydrolinking," utilized high pressure water jets, while "electrolinking" consists of burning out the coal between electrodes placed some distance apart in the seam.[4, 19] Another method for linking the shafts employs a jet of oxygen to facilitate directional burning. Where space in the vertical shafts permits, a number of specialized drills have been developed for the purpose.[13]

The coal surrounding each of the shaft-connecting holes is gasified by starting a fire in the blast inlet shaft at the level of the particular

hole in question, and carrying out combustion of that "crevice" in both directions (from the centre shaft) while the other boreholes are sealed off. The crevices are ignited in succession or in small groups, so that an approximately constant rate of gas production is maintained and the combustion of the coal in the seam is as complete as possible.

As in the stream method, the composition of the gas obtained by the crevice method may be varied within quite wide limits by the use of oxygen and/or steam in the air blast.[3, 9, 12, 18] This method requires a considerable amount of underground work, but it has the advantage of being applicable to horizontal or slightly sloping seams in which the stream method fails because of falling roofs, and also to those seams in which the percolation method cannot develop adequate cracks and fissures in the coal between its shafts. Claims have been made that 80-90 per cent of the coal in a seam can be gasified by the crevice method.[19]

The chief economic advantage said to be offered by underground gasification is the reduction (and possible elimination) of underground labour which it affords. It has been stated that the Russians have increased the average output per man from 30 tons per month by mining methods to the thermal equivalent of 100-200 tons per month by underground gasification.[8, 15] Where gas is the desired product, anyway, another economic advantage is the lesser capital cost of gasification equipment; Russian experience has indicated that the cost of a complete underground-gasification station is only 60-70 per cent of that of an above-ground installation. The cost of power gas produced by underground gasification is said to be about one-third that of similar gas produced in ordinary gasification plants.[7] Where oxygen-enriched blasts are to be used in underground installations, it has been estimated that the cost of the oxygen plant constitutes 70 per cent of the total investment and that the cost of the gas produced is about three times that produced with air alone.[6]

Much of the above must be viewed as indicative rather than conclusive, since the average production of bituminous coal per man-day in the United States was 5.2 tons in 1941,[16] far above the Russian average, while the use of such techniques as strip mining gives even greater man-day yields, such as 14.23 tons in 1938. In any case, the use of underground gasification appears worthy of additional attention.

Work in the United States

What appears to be the first attempt at underground gasification in the U.S.A. is a series of experiments currently being conducted by

the Alabama Power Company in co-operation with the United States Bureau of Mines.[1] The method which is being employed is apparently a special case, adapted only to thin, horizontal veins of coal located near the surface. The plan in question involves "bull-dozing" a 20-foot-wide trench across the coal seam, which is 30-40 inches thick and 40 feet wide. Two parallel shafts, each 6 feet in diameter, will be drilled from this trench, lengthwise with the seam and in a horizontal plane on either side of it; these shafts will then be connected at their extreme ends. One of the shafts will serve as an air (or oxygen) inlet, while the other will act as the gas outlet. The vein will be fired in the connecting shaft, and the seam will be burned toward the cutoff trench. It has been reported that actual tests were scheduled to start early in 1947 and that they may take a year to complete.* The project, the site of which is a new mine at Gorgas, Alabama, is expected to cost about $50,000 to $75,000.

Essentially, the Alabama Power Company's project would seem to consist of a very specialized adaptation of the Russian "stream" method. As mentioned, the stream method is not ordinarily very satisfactory when applied to horizontal or only slightly inclined seams, since the combustion zone becomes obstructed by ash and fallen, unconsumed coal. However, when used to gasify a vein as thin as the one in question, such difficulties are not likely to be encountered.

The open trench of the Alabama method would hardly appear economically feasible where the earth overburden was very thick. Furthermore, in cases where the overburden is light, underground gasification must compete in economy with strip mining. However, the selection for the initial American experiment of a method apparently applicable only to one particular type of coal occurrence may perhaps be justified by the theory of working from the simple to the more complex. At any rate, a start has been made in the United States, and it is certain that future developments will receive careful attention by those interested in the Fischer-Tropsch process, in addition to the gas and coal industries as a whole.

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* Since this was written experiments have been carried out and an account published.[22]

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Chapter 4

SYNTHESIS GAS FROM NATURAL GAS

MIXTURES of hydrogen and carbon monoxide may be produced from natural gas, methane from coal seams, refinery gases, coal carbonization gases, Fischer-Tropsch residue gases, or other gases rich in methane by the following processes:[4, 13, 38]

(1) Reaction with steam, according to the equation:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \ (-201 \text{ B.Th.U.});$$

(2) Reaction with carbon dioxide, according to the equation:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \ (-238 \text{ B.Th.U.}); \text{ and}$$

(3) Controlled oxidation with air or oxygen, according to the equation:

$$2CH_4 + O_2 \rightarrow 2CO + 4H_2 \ (+28.6 \text{ B.Th.U.})$$

The "methane-steam" reaction has been discussed in many articles.[4, 5, 7, 10, 15, 16, 17, 22, 24, 25, 29, 31, 34, 43] This reaction produces a gas which is low in carbon monoxide, but which might, for example, be adjusted to synthesis gas requirements by blending with gas from the reaction of methane with carbon dioxide, since the carbon monoxide content of the latter is high. The two reactions may be carried out simultaneously over a nickel catalyst at a temperature of about 1350° F.,[38] according to the equation $3CH_4 + 2H_2O + CO_2 \rightarrow 4CO + 8H_2$.

According to various investigators, studies of the equilibrium relations of the methane-steam reaction show that, above 1500° F., it is almost entirely confined to the production of hydrogen and carbon monoxide, as long as an excess of steam is avoided. However, with an excess of steam and at temperatures of about 1200° F., the reaction tends to obey the equation $CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$.[4, 23, 35, 37] In the absence of catalysts, the rate of the methane-steam reaction is said to be slow, becoming appreciable only at temperatures above 2370° F.[39]

The U.S. Bureau of Mines has recently investigated the uncatalyzed reaction of natural gas and steam at temperatures up to 2730° F. in order to obtain sufficient data for the construction of a pilot plant.[12] With contact times of 0.21-3.6 seconds, only 1.0-3.2 per cent of the natural gas was undecomposed. Some carbon deposition occurred

in all of the tests, and it was concluded that pilot-plant design must allow for an indeterminate but appreciable amount of carbon deposition. While considerable experimentation appears necessary before the uncatalyzed methane-steam reaction could become a commercial reality, its use for the preparation of synthesis gas might have interesting future possibilities. Pebble furnaces, which provide cheap and efficient heat transfer, might make this high-temperature process feasible.

FIG. 6. *Synthesis-gas pilot plant unit, using natural gas.*
(Courtesy of Phillips Petroleum Co.)

A number of catalysts have been proposed for the reaction of methane with steam, by far the greater number containing nickel promoted and supported in various ways.[4, 5, 15, 28, 31, 34, 43] Among the catalysts which have been suggested are: nickel-alumina-magnesia on active carbon at about 1200° F.;[8] nickel-thoria, magnesia, and nickel-iron at about 1470° F.;[21] nickel-magnesia;[41] 25 per cent nickel, 74 per cent magnesia, and 1 per cent boric acid at 1500-1700° F.;[45] and nickel-alumina on clay.[31] Alumina and magnesia are considered effective activators,[15, 31] while kaolin has been suggested as a support.[31]

Cobalt[4, 15] was found by one group of experimenters[14] to be

greatly inferior to nickel as a catalyst for the reaction at 1650-1830° F. Using a small-scale, intermittent process in which the catalyst was first blasted with a gas-air mixture and the reaction mixture then injected into the catalyst bed, they found that the most reactive and most durable catalysts consisted of nickel deposited on refractory mixtures of alumina and clay, nearly theoretical conversions being reported.

Semi-industrial-scale data on an intermittent, nickel-catalyzed process similar to the one just described showed that, at average temperatures of 1580-1650° F. and 10-minute conversion periods, the average composition of the gas (from natural gas containing about 87.5 per cent methane) was as follows:

	per cent
CO_2	9
CO	22
H_2	64
CH_4	0.8
N_2	4.2

About 0.46 part of natural gas was consumed to produce one part of gas of this composition, approximately 0.30 part actually being converted and 0.16 part being burned to supply heat.[18]

Pilot-plant-scale production of hydrogen-carbon monoxide mixtures from natural gas at 1650-1029° F. using pure nickel stampings $\frac{1}{4} \times \frac{1}{8}$ inch as catalyst has been described by Storch and Fieldner.[40] The gas from this process contained about 75 per cent hydrogen, 21 per cent carbon monoxide, 1 per cent carbon dioxide, and 1 per cent nitrogen + methane.

The petroleum oil hydrogenation plants of the Standard Oil Company of New Jersey at Bayway, New Jersey, and Baton Rouge, Louisiana, reportedly use the methane-steam reaction to produce mixtures of hydrogen and carbon monoxide, utilizing the water-gas shift to eliminate carbon monoxide and obtain the hydrogen required for their operation.[6] Fairly recent improvements in the methane-steam reaction are said to include a continuous conversion process which involves addition of oxygen to the methane-steam mixture and the use of long-lived catalysts.[4, 5] A recent booklet [2] gives some interesting details and estimates based on the use of propane.

Since the reaction of methane with carbon dioxide requires a reactant less readily available, generally speaking, than does the methane-steam reaction, and is even more endothermic than that reaction, less attention has been directed toward its development.

However, this process does have the advantage of giving a gas unusually high in carbon monoxide, and it therefore offers a possibility for increasing the carbon monoxide content of gas from the methane-steam reaction. In this connection, Natta and Pontelli [27] have studied the production of gas mixtures from methane plus steam and oxygen and from methane plus carbon dioxide and oxygen, the oxygen addition being desirable to supply heat of reaction by combustion of part of the charge, as well as for producing the desired gases. These investigators determined the ratio of carbon monoxide to hydrogen as a function of the initial composition of the reactant and the temperature of the reaction for the two ternary systems and for the quaternary system $CH_4 + CO_2 + H_2O + O_2$. Their experiments were carried out in a temperature range of 1470-2550° F. Brassert [44] has patented a process for the production of carbon monoxide from natural gas and gases rich in carbon dioxide, such as blast-furnace or producer gases. There are a number of other references pertaining to this reaction.[4, 13, 15, 28, 30, 32, 43]

Controlled Oxidation

Since it is exothermic and thus does not require expenditures for external heating, the controlled oxidation of natural gas would seem to be more economic than the other processes, provided sufficiently inexpensive oxygen can be obtained. Fischer and Pichler,[9] using two parts of methane to one of oxygen, a temperature of about 2550° F., and a contact time of about 0.01 second, obtained a gas containing about 54 per cent hydrogen, 26 per cent carbon monoxide, 9.4 per cent acetylene, 4.8 per cent methane, and 3.0 per cent carbon dioxide. After removal of acetylene (a valuable product for organic syntheses), this gas would be suitable for use in the standard Fischer-Tropsch reaction without any treatment other than sulphur removal if the latter is necessary. Various catalysts have been proposed for the reaction: nickel at temperatures up to 1830° F.,[26] nickel-magnesium oxide at about 1550° F.,[11] nickel promoted with thoria or silica at about 1650° F.,[19, 33, 42] etc.[4, 28, 30, 32]

The controlled oxidation process has been selected to supply synthesis gas for the Carthage Hydrocol, Inc., Fischer-Tropsch plant at Brownsville, Texas, according to plans recently announced by P. C. Keith.[1, 20, 36] Estimated raw material requirements have been given as 65,000,000 cubic feet of natural gas and 40,000,000 cubic feet of oxygen per day, and it has been said that use of heat from the exothermic synthesis reaction to supply steam to power the compressors will result in a net cost for oxygen of only 5 cents per 1000 cubic feet.

A new method of separating oxygen from the air has recently been publicly announced.[3] In this process, air is blown through a tube lined with a cobalt chelate compound which absorbs oxygen. When the absorption reaches its maximum, the air flow is discontinued and the tube heated to drive off the absorbed oxygen. This process is said to have been used to supply oxygen for welding and other operations in the South Pacific where regular base supplies were not available. Whether the method will prove to have industrial advantages over present large-scale processes for oxygen manufacture remains to be determined, but, if it should turn out to offer an inexpensive source of oxygen, it could vitally affect the economics of a number of chemical processes—among them, the Fischer-Tropsch process.

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Chapter 5

SYNTHESIS GAS PURIFICATION

REGARDLESS of its source, synthesis gas must be almost completely free of sulphur and its compounds for use in the known Fischer Tropsch synthesis processes, about 1 grain per 1000 cubic feet being the maximum tolerable amount.[38] The Robinson-Bindley process of Synthetic Oils, Ltd, is said to employ a sulphur-resistant catalyst which does not require extensive purification of the synthesis gas;[25] but, in general, rigid specifications as to sulphur content have been prescribed.[5, 8, 11, 13, 14, 16, 17, 20, 25, 42] If the synthesis gas is to be produced from natural gas, future practice will probably involve desulphurization of the natural gas prior to its conversion, since smaller gas volumes are thereby handled. The Girbitol process,[7, 12] for example, might well be used, or any of several other desulphurization processes.

The removal of sulphur compounds from synthesis gas is usually accomplished in two steps: (1) removal of the hydrogen sulphide, and (2) removal of the organic sulphur compounds. In the German commercial plants, the removal of hydrogen sulphide was almost universally accomplished by the well-known iron oxide process.[9, 10, 23, 57] However, at least one plant, that at Luetzkendorf, used the "Alkazid" process[32] in which an alkaline organic compound absorbs the hydrogen sulphide and then is steam-stripped for re-use.[9, 36, 57] In all the German plants examined, the organic sulphur compounds were removed by a process which consisted essentially of catalytic oxidation. The gases were passed over a Fe_2O_3-Na_2CO_3 catalyst at temperatures ranging from about 350° F. with fresh catalyst to 535° F. with nearly-exhausted catalyst. Fresh catalyst analyzed 34.4 per cent ferric oxide and 23.8 per cent sodium carbonate, while fully-spent catalyst contained about 33 per cent sodium sulphate, 0.3 per cent sodium sulphite, and 4 per cent sodium carbonate. A small percentage of oxygen in the entering synthesis gas was said to be necessary for removal of the organic sulphur by this process.[9]

The hydrogen sulphide removal process in use at the Steinkohlen-Bergwerk plant was found to consist of passing the gas at atmospheric temperature through a tower containing beds of iron oxide (luxmasse) about 12 inches deep on 18 trays spaced about 40 inches apart. The velocity of the gas through the catalyst was said to be about 3.3 feet per second. According to interrogated Germans, the

catalyst life was about 12 weeks, after which it was discarded. Air was added to the synthesis gas prior to hydrogen sulphide removal to

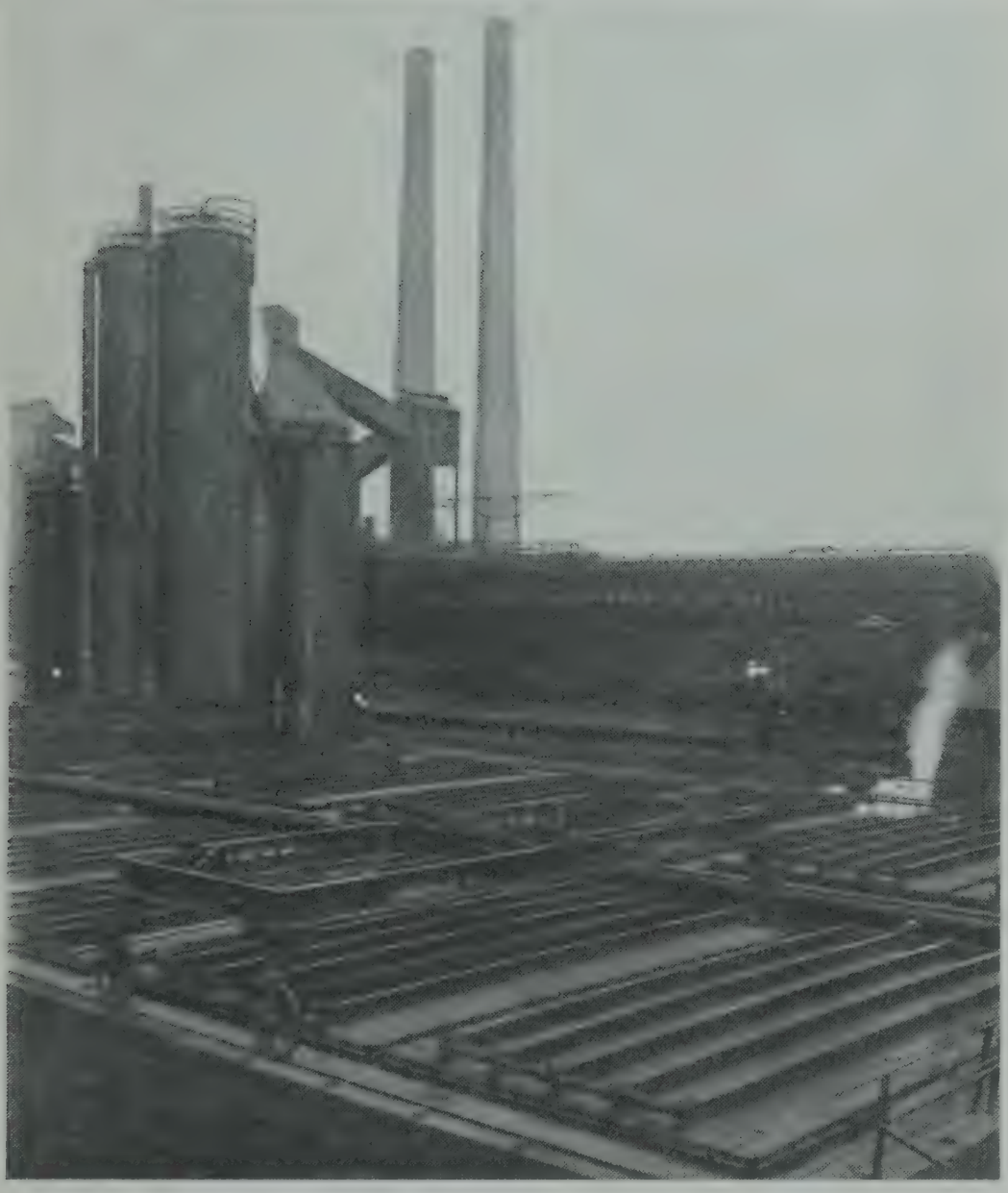

FIG. 7. *Iron oxide gas purifying boxes, with towers in the background for liquid purification of the gas. This process was the one used in Germany for removal of hydrogen sulphide from synthesis gas.* (Courtesy of Koppers Company, Inc.)

function as an oxidizing agent in the subsequent removal of the organic sulphur, which was accomplished in the manner previously described. The total sulphur content of the synthesis gas after purification was said to be about 2 grains per 1000 cubic feet,[10] somewhat

higher than generally considered permissible. The effect of oxygen addition to the synthesis gas (prior to purification) on the removal of both hydrogen sulphide and the organic sulphur is particularly interesting. Hydrogen sulphide removal was said to be poor with only 0.012 volume per cent oxygen; good with 0.177-0.205 per cent, permitting high throughput rates; and seriously decreased when the oxygen content was as much as 0.802-0.903 per cent. The removal of organic sulphur was not satisfactory with oxygen contents as low as 0.012 volume per cent, but was so with 0.177-0.443 per cent. Optimum over-all results were reportedly attained with 0.177 to 0.205 volume per cent of oxygen in the gas.[10]

A number of other processes have been proposed for the purification of synthesis gas. In one multi-stage process, hydrogen sulphide is removed in the first stage by moist iron oxide; a part of the organic compounds are decomposed in the second stage by the action of a mixture of sulphurized iron and an alkali metal carbonate at 570-840° F., the hydrogen sulphide being removed by moist iron oxide; and, in the last stage, the partially desulphurized gas is passed over a mixture of iron oxide and alkali metal carbonate at a temperature of 300-570° F.[35, 50, 54]

The ferric oxide method for removing hydrogen sulphide is well known and long established. A plant employing a mixture of ferric oxide and wood shavings (to give permeability to the mass) has recently be described.[34] Permeability may also be obtained by moulding the catalyst into small balls.[3] The equipment and detailed advantages and disadvantages of the process have been discussed by Turner.[41] The process is said to operate most effectively if the quantity of the gas is small or the hydrogen sulphide content is low. Two good bibliographies on ferric oxide purification of gases have been published recently. The first [21] includes a discussion of test procedures and experimental results, while the second [37] is especially well annotated.

Where the hydrogen sulphide content of the unpurified gas is high, it might prove advisable to remove the major portion by one process, then the remainder by a method (such as that using iron oxide) which gives high removal when the initial content is low. One method for rough removal might utilize the ammonia-Thylox process, which is said to reduce hydrogen sulphide in coke-oven gas from 2500 grains per 1000 cubic feet to less than 80 grains per 100 cubic feet.[6]

Japanese investigators have done considerable experimental work on iron oxide for complete desulphurization of synthesis gas. Iron oxide was found to be effective at about 660° F. and a space velocity of 330 volumes of gas per volume of catalyst per hour.[40] They also

studied the influence of various promoters for the iron oxide catalysts finding that the addition of 10 per cent each of sodium hydroxide and thoria greatly improved the efficiency of the catalyst. At about 660° F., a 7 to 3 mixture of technical iron oxide (luxmasse) and diatomaceous earth with 30 per cent of sodium hydroxide was reported to reduce the sulphur to about 0.35 grain per 1000 cubic feet.[19] The addition of 10 per cent of copper or nickel hydroxides and 10 per cent of sodium hydroxide to luxmasse resulted in a catalyst which, at 390-480° F. and a space velocity of 250 volumes per volume per hour, was said to reduce the sulphur content of synthesis gas to less than 1 grain per 1000 cubic feet.[18]

Removal of both hydrogen sulphide and organic sulphur by reaction over iron oxide catalysts has been claimed by several others.[47, 52, 55, 56] In one of these processes,[55] treatment with active carbon at room temperature prior to passage over the iron oxide is said to remove most of the organic sulphur compounds.

As already mentioned, catalytic oxidation may be employed for removal of the organic sulphur compounds in synthesis gas. In one experiment, in which about 0.6 per cent of oxygen was mixed with the gas and the mixture then passed over a catalyst of nickel hydroxide on china clay, the product (after removal of sulphur dioxide and hydrogen sulphide) contained about 10 grains of organic sulphur per 100 cubic feet.[22]

Underwood [42] has mentioned a "specially prepared nickel catalyst" suitable for the oxidation of organic sulphur compounds to sulphur dioxide, but has not given any details on its use or the results obtained.

Organic sulphur compounds may be subjected to catalytic reduction to hydrogen sulphide, the latter being removed by iron oxide in the usual manner. Processes of this nature are said to permit much higher space velocities than processes using activated iron oxide-alkali catalysts.[38] A pumice-supported catalyst containing uranium and cerium in the ratio of 4 to 1 by weight has been used at a temperature of about 660° F. and a space velocity of 5700 volumes per volume per hour. This process was found to be less effective in removing thiophene than it was in removing carbon disulphide, and it was also observed that the presence of carbon monoxide in the gas being desulphurized reduced the extent of sulphur removal as compared with the desulphurization of pure hydrogen.[1, 27]

Fischer and Tropsch have patented a number of processes for the removal of organic sulphur from water gas, several of them employing catalytic reduction to hydrogen sulphide.[44, 45, 48, 49] Catalysts for the reduction include metals such as lead, tin, and copper mixed

with inorganic bases or acid anhydrides, lead chromate, calcium plumbate, cupric oxide, or lead acetate;[44] and precious metal catalysts, such as silver and gold.[45, 49] Fischer has also patented a process by which the hydrogen sulphide may be removed from the gas after reduction by reaction with an alkaline solution of potassium ferricyanide.[46, 53]

A process for decomposing organic sulphur compounds to hydrogen sulphide by passing the gas at a temperature above 570° F. over a mixture of alkali metal carbonates and iron oxide has been patented by Studien- und Verwertungs-G.m.b.H.[47, 50]

The I. G. Farbenindustrie A.-G. has laid claim to a process for decomposing the organic sulphur compounds to hydrogen sulphide simultaneous with the water-gas-shift reaction, the reaction with steam accomplishing both purposes.[51]

Numerous reviews have recently appeared which include information on the type of sulphur compounds found in gases, their type reactions, determination, and removal.[2, 4, 15, 26, 28, 29, 31, 32, 33, 39, 43] The information on organic sulphur removal published in the period 1930-1942 has recently been summarized,[24] and modern gas-purification plants have been described in some detail.[32] Research is in progress at the Institute of Gas Technology [30] and elsewhere on the development of sulphur-resistant catalysts, since catalysts of this nature would be of considerable economic importance.

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Part II

THE CATALYTIC SYNTHESIS

Chapter 6

REACTION MECHANISMS

ONCE a suitable gas has been prepared, regardless of its source, the next step in the Fischer-Tropsch process is the catalytic synthesis, which consists of the hydrogenation of carbon monoxide over such catalysts and under such conditions that the reaction product consists of paraffins and olefins in varying proportions and of various chain lengths. Depending upon a number of factors, chiefly the ratio of hydrogen to carbon monoxide in the synthesis gas and the type of catalyst employed, one or the other of the following reactions predominates in the synthesis (although both almost always take place to some extent):[29]

$$nCO + (2n + 1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$$
$$nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O$$

The first of these reactions is favoured by relatively high ratios of hydrogen to carbon monoxide and catalysts of strong hydrogenating power, while the second is favoured by low hydrogen-carbon monoxide ratios and catalysts of less strong hydrogenating ability.

When iron catalysts are used instead of those containing nickel or cobalt, the reaction becomes:[13]

$$2nCO + nH_2 \rightarrow C_nH_{2n} + nCO_2$$

As might be expected, since the Fischer-Tropsch reaction is exothermic and involves a reduction in volume, relatively low temperatures and somewhat elevated pressures favour the reaction. The synthesis is generally conducted at temperatures of approximately 375° F. with nickel- or cobalt-containing catalysts and at about 465° F. with iron catalysts. Except in cases where a specific product is desired (such as high-molecular-weight wax), the usual operating pressure lies somewhere between zero and 150 pounds per square inch, gauge. The synthesis gas is passed through reaction chambers in one or more stages, with or without recycle of the unconverted portion;[1] the heavier products are condensed from the residual gas; and the lighter products are adsorbed on charcoal (in the atmospheric synthesis) or absorbed in oil (in the medium-pressure synthesis). Considerable variations in the quantity and types of products

are obtained under different reaction conditions, as will be shown in subsequent chapters of this book. However, prior to a discussion of the effect of the reaction variables, it might prove instructive to review the theories advanced on the mechanism of the process and to mention the various types of catalysts which may be employed.

Many of the theories regarding the reaction mechanisms of the Fischer-Tropsch process stipulate the intermediate formation and decomposition of carbides of the catalyst metals. It has been shown that iron, cobalt, nickel, and ruthenium (those metals which best catalyze the reaction) all possess the common property of forming relatively unstable carbides of nonionic crystalline structure when exposed to carbon monoxide at temperatures within the range employed in the Fischer-Tropsch process.[15] Below about 660° F., these carbides will react with hydrogen, being quantitatively converted to methane plus a small amount of ethane.[2, 3, 4] However, at temperatures above 660° F., the carbides tend to decompose to carbon.[26] In view of this behaviour of the carbides of Fischer-Tropsch-catalyst metals, it may be interesting to note that the optimum temperature ranges for the synthesis reaction lie below 660° F., the temperature above which the carbides break down to carbon.[26]

Fischer[14] has long been of the opinion that methylene radicals, $(CH_2)_n$, are formed when the carbides are treated with hydrogen and that the products of the synthesis are formed by the combination of these radicals into chains of various lengths and degrees of saturation. At least as late as 1935, he was not willing to choose between two possible explanations for the mechanism of methylene-radical formation from the catalyst carbides.[14] He assumed either: (1) that the normal carbide, Me_3C, is formed in the presence of carbon monoxide and then reduced by hydrogen to the metal, giving rise to methylene radicals, or (2) that the normal carbide, Me_3C, is carbonized to a higher carbide, Me_3C_2, which, upon reduction to the normal carbide, forms the methylene radicals. According to Fischer's beliefs, this step of the reaction with nickel or cobalt catalysts may be represented by the equation:

$$CO + 2H_2 \rightarrow (CH_2) + H_2O\,(+\ 175\ \text{B.Th.U.})$$

and, with iron catalyst, by the equation:

$$2CO + H_2 \rightarrow (CH_2) + CO_2\,(+\ 173\ \text{B.Th.U.})^{13}$$

Fischer's reasoning may be summed up as follows: since only those Group 8 metals which are known to react with carbon monoxide at temperatures near 390° F. are suitable as Fischer-Tropsch

catalysts, and since the carbides of those metals are found in the spent catalysts, it appears that carbides are formed by the interaction of the catalytic metals with carbon monoxide and that the methylene radicals are produced by secondary hydrogenation of these carbides.[11, 12] In 1938, Fischer reiterated his assumption that the mechanism may involve the alternate formation of higher and lower carbides.[13]

As mentioned in the first chapter, one of the current theories presupposes that the catalyst, in addition to giving rise to methylene radicals, also influences both their polymerization to hydrocarbons and the subsequent hydrogenation of these hydrocarbons.[28] Experiments reported by Herington and Woodward[19] indicate that two types of active centres are present on the surface of a Fischer-Tropsch cobalt catalyst. The Type A centre (probably cobalt carbide) is considered responsible for the formation of methylene radicals and their polymerization to hydrocarbons. The Type B centre (probably metallic cobalt) is believed to provide the surface upon which the hydrogenation and chain-liberation occurs. "The predominance of one or the other type of centre explains some of the problems of preliminary methane formation and catalyst poisoning."[28]

Komarewsky and Riesz[20] are also of the opinion that Fischer-Tropsch catalysts must possess both a polymerizing and a hydrogenating effect, in addition to the ability to form carbides of suitable stability. They have pointed out that nickel, cobalt, and iron form suitable carbides and possess hydrogenating ability: when pure nickel is used as catalyst, however, only methane is formed in the synthesis step, and hydropolymerization to form higher hydrocarbons does not take place. In such cases, a multicomponent, "complex-action" catalyst seems required; this theory is further supported by the fact that the catalyst compositions most favoured for the Fischer-Tropsch reaction are, as mentioned, composed of several elements.

Experiments reported by Craxford and Rideal have seemed to indicate that the reaction between carbon monoxide and cobalt to form cobalt carbide is far too slow to explain the rate of synthesis of hydrocarbons from hydrogen-carbon monoxide mixtures.[6, 8] However, recent tests conducted by the United States Bureau of Mines indicate that the rate of carbiding is of the same order of magnitude as the synthesis rate.[27] Craxford's suggested mechanism for the cobalt-catalyzed synthesis assumes that the first step is the reaction of both carbon monoxide and hydrogen to form the carbide:

$$2Co + CO + H_2 \rightarrow Co_2C + H_2O$$ [6, 8]

This reaction (which occurs more rapidly than carbiding with carbon monoxide alone) involves: (1) chemisorption of carbon monoxide on the catalyst, (2) reduction of the chemisorbed carbon monoxide by hydrogen to give the carbide, and (3) reduction of the carbide by molecular hydrogen to chemisorbed methylene. In all their experiments, Craxford and Rideal noted a parallel relationship between ortho-para hydrogen conversion and methane formation. When methane was the main product, the ortho-para conversion was high (an indication of the presence of chemisorbed hydrogen); conversely, when higher hydrocarbons were being produced, the ortho-para conversion amounted to only a few per cent. This led them to the belief that a relationship may exist between the quantity of chemisorbed hydrogen on the catalyst surface and the products of the synthesis; i.e., that, in the presence of a large amount of chemisorbed hydrogen, methane is formed from the reaction; while in the presence of smaller quantities, reduction of the carbide (presumably by molecular hydrogen) occurs, with the production of higher hydrocarbons. The latter step may occur through the formation of polymethylene macromolecules on the catalyst surface, their reduction by molecular hydrogen, and their sybsequent desorption.

Storch [26] has pointed out the possibility that hydrogen may catalyze the formation of metal carbides by forming an unstable metal hydride. "This may result in sufficient distortion of the metal lattice so that, upon removal of the hydride hydrogen (by decomposition or by reaction with neighbouring metal carbide or adsorbed carbon monoxide), penetration of the lattice by carbon monoxide is accelerated." The fact that iron catalysts sintered in hydrogen at 1560° F. are quite active is pointed out by Storch[27] as lending weight to the premise that only a very small fraction of the catalyst surface possesses the critical spacing of metal atoms which is necessary to facilitate the synthesis reaction.

Two possibilities exist in the formation of Fischer-Tropsch products from methylene radicals: (1) either a very large molecule may be formed which is then cracked to yield the observed products (of various chain lengths);[6] or (2) polymerization may result directly in chains of the lengths ultimately collected, without the intervention of cracking.[17] Herington, in a recent paper,[18] has discussed the reaction from the standpoint of the second (direct polymerization) possibility.

According to Herington, chain initiation may occur: (1) from suitable activation of a methylene radical, or (2) from a methyl radical formed by the attack of a hydrogen atom on a methylene radical. Addition of methylene groups then propagates the chain. If

the chain grows from only one end, termination will result in the formation of an olefin with a terminal double bond.

An olefin is produced if a chain initiated by a methylene radical leaves the catalytic surface. However, before a chain initiated by a methyl radical can become an olefin it must lose a hydrogen atom. This may be a direct loss; may occur through mutual termination between two radical chains, with the loss of a hydrogen molecule; or it may occur through disproportionation between two radical chains to give an olefin and a paraffin, respectively. The hydrogen atom might also attach itself to a methyl radical, yielding one molecule of methane for every molecule of product of chain length greater than C_1. The paraffins are produced either by hydrogenation of the olefins or by hydrogenation of the radical chains. Herington's hypothesis that each ultimate molecule of nCH_2 units has at one time been of length 1 to n units, but never has been of m units where m is greater than n, enables him to employ the β function method to analyze distribution curves. Thus,

$$\beta n = \frac{\text{Probability of escape of radical } n \text{ from reaction zone}}{\text{Probability of its appearing in products as chain} > n}$$

$$= \frac{\text{Yield of chain length } n}{\text{Sum of yields of chain length} > n} \tag{1}$$

while the probability of radical of length n appearing in the product as a chain of length n can be considered as composed of two parts: (1) probability of appearing as paraffin, $\phi(H)$; and (2) probability of appearing as olefin, $\phi(O)$. Representing the probability of propagation and of occurrence of the radical in the product as a longer chain, $\phi(P)$,

$$\beta n = \frac{\phi(H) + \phi(O)}{\phi(P)} \tag{2}$$

Now the mol fraction (u) of chain length (n), which is olefinic, is by definition:

$$u = \frac{\phi(O)}{\phi(H) + \phi(O)} \tag{3}$$

Eliminating $\phi(O)$ and $\phi(H)$ from equations (2) and (3) gives

$$\frac{\phi(H)}{\phi(P)} = \beta(1-u) \tag{4}$$

and

$$\frac{\phi(O)}{\phi(P)} = \beta(u) \tag{5}$$

The third ratio is by definition

$$\frac{\phi(O)}{\phi(H)} = \frac{u}{1-u} \tag{6}$$

"The above equations do not assume a steady state condition. In practice, the amount of radical is small compared with the amount of product so that the probability of a radical of length n appearing in the products as a hydrocarbon of length greater than n, (i.e. $\phi(P)$) is very nearly equal to the probability of a radical n growing to a radical of longer chain length. This is true even if a steady state is not reached while, under these conditions, equation (7) (which follows) is also approximately correct.

"If, however, a steady state is reached, (and for many catalysts this probably obtains), then the close approximation between the probabilities of growing and appearing in the product becomes an equality and, in addition,

$$\phi(O) + \phi(H) + \phi(P) = 1 \tag{7}$$

which enables the individual values of $\phi(O)$, $\phi(H)$, and $\phi(P)$ to be calculated using equations (4), (5), and (7)."[18]

Craxford, who believes that the hydrocarbon products of the reaction are formed from very long methylene polymers by hydrogenation-cracking, has recently reported some very interesting experiments[7, 31, 32] which tend to support his theory. With a cobalt-thoria-magnesia-kieselguhr catalyst, he found that the oil yield is a maximum at a gas rate of approximately one litre per gramme of cobalt per hour and that the amount of carbon dioxide formed is small for higher rates but increases rapidly at lower rates. This would indicate that at low gas rates only the front section of the catalyst bed (where the cobalt has been largely converted to carbide) is

engaged in oil synthesis, while the second part of the bed, not needed for the oil synthesis at low gas rates and relatively free from carbide, is available for the water-gas-shift reaction and hydrogenation-cracking of the higher hydrocarbon products to methane. At the rate for maximum oil yield, the entire catalyst bed is actively engaged in oil synthesis and little opportunity is provided for the secondary reactions of carbon dioxide formation and degradation to methane. The oil yield also falls off at gas rates greater than the optimum, since the synthesis gas is not left in contact with the catalyst long enough for the oil-forming reaction to go to completion.

In his experiments, Craxford observed that the low oil yields at low gas rates were accompanied by "abnormally large" methane production, the decrease in oil being almost exactly equal to the increase in methane. In order to test his theory that this methane is formed by hydrogenation-cracking of the synthetic oil on the non-carbided portion of the catalyst, he conducted the synthesis reaction in an apparatus with two catalyst beds in series. Using only the first bed, an oil yield of 122.5 grammes per cubic metre of synthesis gas was obtained. However, when the gas rate was left unchanged and the residual gas and oil vapours from the first catalyst chamber were passed through the second catalyst bed, the oil yield fell to 102.2 grammes per cubic metre. Moreover, passage of hexane vapour over freshly reduced catalyst at 365° F. showed that cracking to methane occurs at a rate more than sufficient to account for methane formation at the expense of oil yield when low gas rates are employed.

Craxford's experiments suggest a convenient method for estimating the activity of a Fischer-Tropsch catalyst—by measuring the gas rate at which the water-gas-shift reaction sets in; the more active the catalyst, the higher the rate. They also indicate two advantages to conducting the synthesis in stages: (1) the oil removed from the first stage is protected from hydrogenation-cracking, and (2) the increased partial pressure of carbon monoxide occasioned by removal of already-formed oil vapour promotes the formation of catalytic carbide and thereby increases oil synthesis and suppresses secondary formation of methane in the later stages.

The fact that only a small amount of carbon dioxide is formed at the gas rate at which the oil yield is a maximum indicates that carbon dioxide is not an integral part of the primary Fischer-Tropsch reaction, such as $2CO + 2H_2 \rightarrow CO_2 + -CH_2$, but is a separate (water-gas-shift) reaction of a secondary nature. The oil-forming reaction would therefore appear to be $CO + 2H_2 \rightarrow H_2O + -CH_2$, followed when conditions permit by the water-gas-shift reaction.[7]

Summing up what is known or assumed of the reaction mechanism of the Fischer-Tropsch process, and attempting to explain the synthesis reaction in the light of the carbide-methylene radical theory, carbide formation would seem to be the first step, followed by establishment on the catalyst surface of a "steady state" which involves polymerization, reduction, and desorption of the methylene and polymethylene groups, the extent of the polymerization being determined by the rate of desorption. Low conversion of the catalyst metal to its carbide and/or a rapid rate of desorption of the methylene groups cause a low concentration of methylene groups on the catalyst surface, and polymerization is consequently retarded. Under these conditions, methane is the main product, and ample active surface is provided on the catalyst surface for ortho-para hydrogen conversion. The high production of methane (to the exclusion of higher hydrocarbons) which is experienced when breaking in a new catalyst may be explained by the necessity for covering the catalyst surface with polymethylene groups to slow up the reduction of the methylene radical to methane. The accelerated rate of desorption of methylene groups at higher temperatures might account for the fact that methane production predominates at temperatures above 480° F.[25]

The reaction mechanism proposed by Matsumura, Tarama, and Kodama[21] assumes the transient existence of the metal oxide in the catalyst-carbiding step and the subsequent formation of chemisorbed water by the reduction of this oxide with hydrogen from the synthesis gas. These investigators consider the first step of the reaction to be:

$$CO + 3Me \rightarrow Me_2C + MeO$$

Their explanation for the formation of hydrocarbons is not markedly different from those of the catalyst-carbide theories previously discussed. However, the interesting feature in their theory is the explanation it affords for the formation of water as a reaction product of the synthesis over cobalt, and of carbon dioxide from the reaction over iron. They believe that:

(1) Through combination with atomic hydrogen adsorbed on the catalyst, the carbide forms methylene groups which, during their residence upon the catalyst, are polymerized, reduced, and converted into hydrocarbons. The hydrocarbons so formed, present in the adsorbed state on the catalyst, eventually become desorbed. The three processes (polymerization, reduction, and desorption) occur successively in respective order, attaining a sort of "steady state" in which hydrocarbons of various molecular weights are produced.

(2) Hydrocarbons of the gasoline range are formed over cobalt catalysts at temperatures above 320° F. because only above this temperature are sufficient quantities of active hydrogen adsorbed on the catalyst.

(3) The higher reaction temperature required when iron catalysts are used may be explained by the fact that the temperature of formation of iron carbide from the metal and carbon monoxide is greater than that for cobalt carbide formation.

(4) The subsequent reduction with hydrogen of the metal oxide formed in the catalyst-carbiding step gives rise to water which is chemisorbed on the catalyst surface. With cobalt catalysts, the rate of desorption of chemisorbed water is greater than with iron catalysts. Thus, in the case of the reaction over cobalt, the chemisorbed water is rapidly desorbed and appears as a reaction product. However, when iron catalysts are used, there is greater opportunity for the carbon monoxide in the synthesis gas to form carbon dioxide by reaction with the metal-oxide areas on the catalyst surface, accounting for the appearance of carbon dioxide in the reaction products.

Elvins and Nash[10, 22] apparently were the first to suggest a Fischer-Tropsch reaction mechanism involving oxygen-containing intermediates. Smith, Hawk, and Golden,[24] somewhat later, passed acetone and acetone plus hydrogen over a cobalt-copper-manganese oxide Fischer-Tropsch catalyst in an attempt to determine whether acetone was an intermediate in the reaction. However, the hydrocarbons which they obtained were different in character from those usually produced from hydrogen and carbon monoxide.

Using Balandin's multiple theory of catalysis,[5] Eidus has suggested a reaction mechanism involving the intermediate formation of methylene radicals without assuming the presence of catalyst carbides.[9] This mechanism may involve adsorption of carbon monoxide and hydrogen on the catalytic surface, interaction to form an oxygen-containing hydrogenation product, and further hydrogenation to the methylene radical and water. In order to investigate the likelihood of their being intermediates in the synthesis of hydrocarbons, Eidus passed methanol, ethanol, and formic acid, separately, over a conventional cobalt-thoria-kieselguhr catalyst at 338-392° F. While liquid hydrocarbons were found in the products from each experiment, the quantities and types of hydrocarbons produced indicated that they had probably been formed from carbon monoxide and hydrogen resulting from decomposition of the organic compounds rather than from further reaction of these compounds over the catalyst. Apparently, then, methanol, ethanol, and formic acid

are not to be considered intermediates in the formation of methylene radicals.

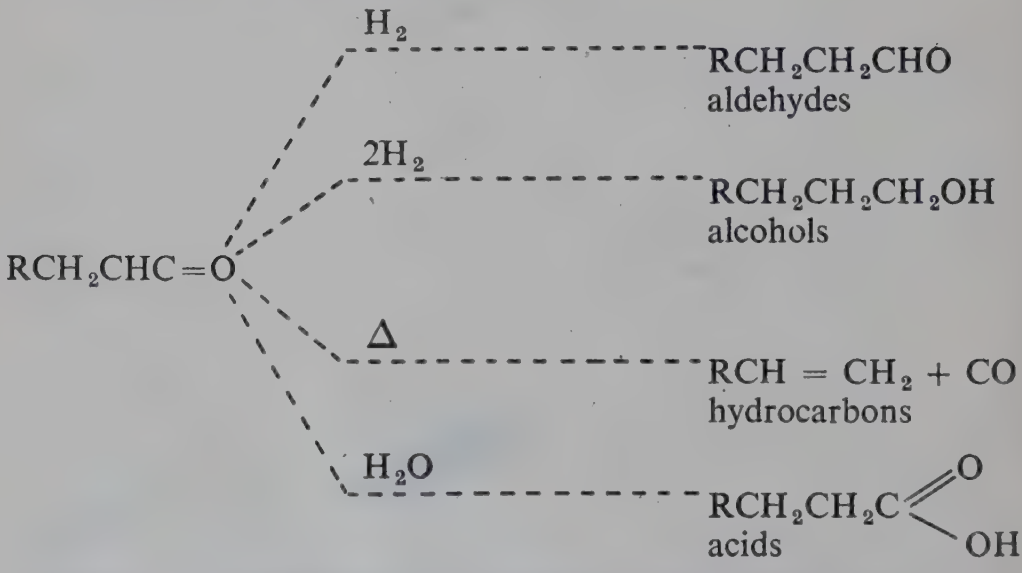
Similar experiments with ketene have recently been reported by Warner, Derrig, and Montgomery.[30] From a typical experiment charging 7.35 litres of hydrogen and about 16 grammes of ketene, the following weight balance was obtained:

Product	*Weight, grammes*	*Weight per cent yield**
Methane	0.38	2.76
Ethylene	0.37	2.69
Propylene	0.52	3.78
Total liquid	3.00	21.82
Wax	0.50	3.64
Carbon monoxide	8.82	64.15
Total	13.59	98.84

* Based upon 13.75 grammes of reacting ketene.

"A reasonable assumption to explain the experimental results involves preliminary catalytic decomposition of ketene, $CH_2CO \rightarrow CH_2 + CO$, followed by polymerization of methylene, $nCH_2 \rightarrow (CH_2)_n$, or by reactions such as $n(CH_2) + CH_2CO \rightarrow CH_3(CH_2)_{\overline{n-1}}CH{=}C{=}O$, and $CH_3(CH_2)_{\overline{n-1}}CH{=}C{=}O \rightarrow CH_3(CH_2)_{\overline{n-2}}CH = CH_2 + CO$.

"The latter reactions involving higher ketenes are favoured, since they could account for the presence of oxygenated compounds in the Fischer-Tropsch synthesis as follows:



Formation of ketenes would be favoured at high pressures where the CO concentration on the catalyst would be high. . . .

"Assuming that the formation of hydrocarbons from ketene proceeded stepwise in the following manner,

(a) $CH_2CO \rightarrow CH_2 + CO$

(b) $CH_2 + CH_2CO \rightarrow CH_3CH{=}C{=}O$

(c) $CH_3CH{=}C{=}O \rightarrow CH_2{=}CH_2 + CO$

(d) $CH_2 + CH_3CH{=}C{=}O \rightarrow CH_3CH_2CH{=}C{=}O \rightarrow CH_3CH{=}CH_2 + CO$, etc.,

a reaction mechanism for the Fischer-Tropsch synthesis may be formulated from the above reactions by providing a source of methylene radicals. Such a source might be the usual one from metal carbide and hydrogen or that postulated by Eidus."

That the initial step in the Fischer-Tropsch reaction is the adsorption of carbon monoxide on the surface of the cobalt catalyst, forming $Co-Co(-C{=}O)Co$, which is reduced first by adsorbed hydrogen to $Co-Co(-HCOH)Co$ and then to $Co-Co(-CH_2)Co$ has been suggested by Hamai.[16] Free migration of methylene radicals on the catalytic surface is assumed to take place, the radicals polymerizing with each other to form $Co-Co(-CH_2-CH_2-CH_2-CH_2-)Co$. Then, upon desorption, radical chains of the form $(CH_2)_n$ are released and are hydrogenated to the final products.

In place of the theory of the polymerization of methylene radicals to explain the formation of long-chain hydrocarbons in the Fischer-Tropsch process, Robinet[23] has proposed a theory involving copolymerization at active centres. He believes that primary (oxygen-containing) complexes are initially formed on the catalyst. In the presence of condensing catalysts, an increase in the complex occurs on certain active centres, the reaction becoming strongly exothermic. The growth of the complex is terminated by dehydration or decarboxylation. Since it appears probable that the complex grows under the influence of free radicals that originate simultaneously on other active centres as well as under the influence of carbon monoxide and hydrogen, the last step might be considered copolymerization upon active centres.

A knowledge of reaction mechanisms is of vital significance to the use of any process, for it makes possible the prediction of results from reasonable variations. From the amount of study given to the Fischer-Tropsch process, it would appear likely that a reasonably complete reaction theory will soon be evolved—possibly a combination of several of those presented here, for the Fischer-Tropsch process is by no means a single, simple reaction of carbon monoxide and hydrogen.

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Chapter 7

CATALYSTS

THE catalytic metals used by Fischer and Tropsch in their early experiments were iron and cobalt, the former being activated with copper and alkali and the latter with zinc oxide. Their experience using nickel was disappointing, and they attributed this fact to the known powerful hydrogenating influence of nickel, believing that it caused direct hydrogenation of the carbon monoxide to methane. However, they later found nickel to yield hydrocarbons when combined with other catalytic materials.[11] In the light of the theory that a Fischer-Tropsch catalyst must encourage both polymerization and hydrogenation, the failure of nickel alone to catalyze the synthesis of higher hydrocarbons might be explained, as mentioned, by its lack of polymerizing ability.

While admixture with other catalytic or activating materials is necessary in the case of nickel, it is also highly desirable in the case of the other catalytic metals. The added materials may serve one or more of the following purposes; they may: (1) supply a catalytic effect not possessed by the catalytic metal alone; (2) activate or promote the catalyst; (3) facilitate catalyst preparation, conditioning, or regeneration; (4) inhibit catalyst poisoning; (5) improve the physical nature of the catalyst; and/or (6) provide a support for the catalytic metal. Superior results have been obtained with those multicomponent catalysts in which (1) each component has been selected for its particular effect upon the reaction, and (2) the relative proportions of these components have been adjusted to give composite masses capable of directing the synthesis toward the production of hydrocarbons of desired molecular weight and structure. The practical application of the Fischer-Tropsch process already requires "complex-action" catalysts,[26] and it would logically appear that the development of modifications of the process to yield special-type hydrocarbons will, in the future as in the past, depend largely upon the results of catalyst research and development.

The choice of the catalytic metal has, in itself, a definite influence on the degree of saturation of the products of the synthesis. Cobalt is intermediate in hydrogenating power, its replacement by nickel in Fischer-Tropsch catalysts leading to the formation of more saturated products, and its replacement by iron resulting in greater yields of olefins.[11]

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The theoretical yield from one cubic metre of "ideal" synthesis gas ($2H_2 + 1CO$) is 208 grammes (about 13 pounds per 1000 cubic feet). However, in actual practice, the synthesis gas always contains a considerable quantity of inert materials (carbon dioxide, nitrogen, methane, etc.); for this reason, even with a catalyst giving total conversion, the yield will rarely exceed about 180 grammes (11.2 pounds per 1000 cubic feet).[40]

If any very large quantities of the so-called "inert" materials are present in the synthesis gas, there is some reason to believe that they may exert a depressant effect on the synthesis of liquid products in addition to one of simple dilution. Murata and Yamada[33] state that ammonia and oxygen in concentrations of less than 10 per cent greatly reduce the gasoline yield over an iron-copper-kieselguhr-potassium hydroxide catalyst. Carbon dioxide is said to exert a similar, but weaker, retarding effect, and nitrogen and methane are said to be still weaker depressants.

The more active Fischer-Tropsch catalysts consist of mixtures of cobalt and/or nickel with activating materials such as alumina, thoria or other difficulty-reducible metal oxides. These catalysts give fairly high yields (up to about 170 grammes per cubic metre) at temperatures of about 374° F. Recent experiments with iron catalysts have shown that at higher temperatures and pressures, such as 465° F. and 150 pounds per square inch, yields may be obtained which are comparable in quantity to those from cobalt or nickel complex catalysts.[43]

Supported Nickel Complex Catalysts

Complex catalysts containing nickel or cobalt as the prime catalytic metal and other elements and compounds as supplemental catalytic agents are generally prepared by coprecipitation of the chemically active ingredients upon the inert carrier. One such method involves the addition of alkali carbonates to solutions of the nitrates of the desired components in the presence of sufficient kieselguhr to serve as a support. During the precipitation, the kieselguhr is kept in suspension by mechanical agitation; the mixture is then filtered, washed, dried, and reduced with hydrogen. In the case of nickel-manganese-alumina catalysts, carrying out the precipitation in the presence of ammonia is said to increase the yield in the subsequent synthesis step and to lower the temperature for optimum reduction of the catalyst from about 840° F. to 570-660° F.[14]

Catalysts consisting of 100 parts nickel; 20 parts manganese oxide; 4-8 parts thoria, alumina, tungstic oxide, or uranium oxide; and 125 parts kieselguhr have been found to yield from 0.75-1.2

gallons of liquid hydrocarbons per 1000 cubic feet of synthesis gas at temperatures of 365-410° F. and a space velocity of about 150 volumes of synthesis gas per volume of catalyst per hour.[18, 22, 58]

In its search for a longer-lived catalyst, Robinson-Bindley Processes, Ltd (now known as Synthetic Oils, Ltd) developed a nickel-manganese-alumina catalyst precipitated on kieselguhr. This catalyst was additionally supported by grinding it, moistening it with a partly hydrolyzed solution of ethyl orthosilicate in toluene, and extruding it in rods through a $\frac{1}{4}$-inch nozzle. Upon exposure to moist air for several days, the hydrolysis of the ester was complete, and a porous silica-kieselguhr-supported catalyst was obtained.[1, 8]

Fischer early patented complex nickel catalysts prepared by the coprecipitation technique, specifying thorium, aluminum, and cerium compounds as suitable activating materials.[62, 79] Russian investigators have also studied complex nickel catalysts.[23, 38]

Supported Cobalt Complex Catalysts

Kieselguhr-supported mixtures of cobalt and thorium oxide (and/or other activating materials) were the "standard" catalysts for the German Fischer-Tropsch process.[96, 99] Such catalysts give high yields of primary product and, in their present state of development, possess fairly long active lives.[97] The catalyst used exclusively by the Germans in their commercial-scale Fischer-Tropsch plants during the late war was of this type, and a description of its composition, preparation, conditioning, regeneration, and reworking may be found in reports of Allied investigations in Germany.[96, 99, 100] According to one interrogated German, "it has been possible in a modern synthesis plant (using the wartime catalyst) to produce 168 grammes of primary product per cubic metre of synthesis gas, and also to obtain approximately 94 per cent of the theoretical yield of 180 grammes (from synthesis gas containing inerts)."[61] Expressed in English units, this is a yield of 10.5 pounds per 1000 cubic feet out of a possible 11.2 pounds.

In 1935, after testing "several hundred" catalysts, Fischer[11] stated that cobalt-thorium-kieselguhr catalysts had given the best results up to that time. He also reported that the addition of two per cent of copper to the catalyst greatly increased the ease of reduction of the catalyst. The experiments of Fischer and his co-workers with the cobalt-copper-thorium oxide-kieselguhr catalyst have been reported by both Koch and Pichler.[24, 34]

Several Japanese investigators have studied kieselguhr-supported cobalt catalysts, reporting quite high yields from compositions consisting of 5-10 per cent of copper, 4-12 per cent of manganese

oxide, and 4-12 per cent of thoria, alumina, or uranium oxide.[18,22,58]

As mentioned, all commercial-scale Fischer-Tropsch operations in Germany appear to have been conducted over a more or less standard type of cobalt-thoria-magnesia-kieselguhr catalyst.[5] Upon questioning, a number of German technical men maintained that all synthesis plants in Western Germany were supplied with a catalyst containing 100 parts cobalt, 5 parts thorium oxide, 8 parts magnesium oxide, and 180-220 parts kieselguhr.[5, 6] However, a tentative analysis of what was said to be fresh catalyst obtained from Ruhrchemie at Oberhausen-Holten indicated 8.8 parts thorium oxide, 4.4 parts magnesium oxide, and 260-330 parts kieselguhr to every 100 parts of cobalt.[6]

Magnesia-containing catalysts are said to have been in use since 1938, their introduction having made possible catalyst lives of up to eight months at normal pressure.[6] According to Dr F. Martin,[96] managing director of Ruhrchemie A.-G., the magnesia was added solely to increase the hardness of the resulting catalyst and thus to reduce its tendency to disintegrate to dust in the ovens, since such dust causes bad gas distribution and leads to "hot spots". Martin stated that catalysts containing the full amount of thoria produced more paraffin and that the substitution of magnesia decreased this production, it being necessary to strike a compromise between the relative proportions of thoria and magnesia in order to obtain a catalyst giving high production and possessing good physical strength. Prof. Dr Alberts, director at Castrop-Rauxel and former manager of the Sterkrade-Holten plant, said that the incorporation of magnesia in the catalyst also contributed to the ease of initiating the synthesis and to the depression of methane and carbon formation.[5, 96]

The kieselguhr used in such catalysts reportedly must contain less than one per cent of iron or excessive methane production will be obtained during the synthesis. Its content of uncalcined aluminum trioxide also must be low (0.4 per cent or less), otherwise the catalyst tends to gel. German practice was to calcine the kieselguhr,[99] prior to use, at 1100-1300° F., after which it should not contain over one per cent total volatile matter, including water. Although the iron in the kieselguhr may be removed by acid treatment, it was believed that the advantage gained by the iron removal is overbalanced by the loss of desirable physical structure when acid treatment is employed.[5]

The catalyst was prepared from a solution of the corresponding nitrates (in suitable proportion) by precipitation at about 212° F. with sodium carbonate.[96] After washing, drying, and screening, the

finished catalyst particles were 1-3 millimetres (0.04-0.12 inch) in size and had a bulk density of 320-350 grammes per litre (20-21·8 pounds per cubic foot). Reduction of the catalyst was reportedly effected by treating it with ammonia synthesis gas (hydrogen, 75 per cent, nitrogen, 25 per cent) preheated to about 860° F. at a space velocity of around 8800 for some 40-60 minutes. Optimum regeneration conditions were said to be difficult to determine; in general, the lower the reduction temperature the better, but lower temperatures require the use of longer times.[5] A similar process of catalyst manufacture (carried out at the Courrières-Kuhlman plant at Harnes, France) has recently been described in some detail.[40]

According to the information obtained, the spent catalyst from all Western Germany's synthesis plants was returned for reworking to Ruhrchemie at Sterkrade-Holten, the plant where it was produced.[5] The components of the spent catalyst were converted to the corresponding nitrates by reaction with nitric acid (about 36° Baumé), then treated to recover the cobalt and thorium. The magnesium was discarded, since its value was not considered great enough to warrant the effort of purification. Details of the catalyst recovery operation have been outlined by Aldrich.[2, 40]

While it has long been known that cobalt, thoria, and kieselguhr in the proportions 100:18:100 comprise one of the better catalysts for the Fischer-Tropsch reaction, little or nothing (aside from conjectures) has been published on the functions of the thoria and the kieselguhr in such a catalyst. In order to investigate this subject, Craxford[9] has recently measured the rates of the simple reactions which (according to the carbide-methylene radical theory) form the first steps in the synthesis for the following five catalysts: (1) cobalt alone; (2) cobalt-thoria, 100:18; (3) cobalt-kieselguhr, 1:1; (4) cobalt-thoria-kieselguhr, 100:18:100; and (5) cobalt-thoria-kieselguhr, 100:21:100. In the first series of tests, made to determine their activity as hydrogenation catalysts, all five were found to be equally active in the reduction of ethylene to ethane at 68° F. This suggested to Craxford that the available area of the cobalt may be the same in all the catalysts, that neither the thoria nor the kieselguhr causes an increased dispersion of the cobalt, and that neither thoria nor kieselguhr is a specific promoter for the reduction of olefins.

Measurement of the rate of carbide formation of the five catalysts indicated that "both kieselguhr and thoria are powerful specific promoters for this reaction, that the most effective catalyst is that containing 18 per cent thoria and no kieselguhr, and that the catalyst with 21 per cent thoria reacts much more slowly than the active

Fischer catalysts with 18 per cent thoria, both containing kieselguhr."

Thoria and kieselguhr were also found to be strong promoters for the reaction of hydrogen with cobalt carbide to yield methane (presumably by way of methylene groups). However, it seems significant, that of all five catalysts tested, the 100: 18: 100 catalyst gave by far the slowest rate of reduction of the carbide, with the exception of the pure cobalt catalyst. This agrees with that part of the theory which stipulates that, for a good Fischer-Tropsch catalyst, the rate of formation of the carbide must be greater than the rate of carbide reduction in order to exclude large quantities of chemisorbed hydrogen from the catalyst surface (with consequent methane formation and occurrence of the water-gas-shift). "The preparation with cobalt-thorium oxide 100 : 18 has a very high rate of carbide formation, but it is not a good Fischer catalyst because it shows too high a rate of reduction of carbide. It should form a much better Fischer catalyst than the usual ones if some means were discovered for decreasing the rate of reduction of its carbide by the desired amount. The preparation with cobalt-thoria-kieselguhr 100: 21: 100 is poor in two respects; firstly that its rate of carbide formation is slow compared with the normal active Fischer catalyst, and (secondly) its rate of carbide reduction is high."

On the basis of these experiments, Craxford concludes: (1) that thoria and kieselguhr do not act primarily by increasing the available area of the cobalt, but rather as specific promoters for the formation and reduction of cobalt carbide, and (2) that the primary requirement that an active Fischer-Tropsch catalyst must have a high rate of carbide formation is inseparably coupled with the requirement that it have a relatively slow rate of carbide reduction.[9]

Supported Cobalt-Nickel Complex Catalysts

As previously mentioned, cobalt catalysts give lower methane yields and more olefins in the product than do nickel catalysts. However, about 50 per cent of the cobalt may be replaced by nickel without loss of these advantages.[54] In his experiments with precipitated catalysts containing equal parts of cobalt and nickel as the prime catalytic agents, Tsutsumi[56, 57, 59, 60] obtained very low yields without the use of promoters. His most satisfactory catalyst contained 20 per cent manganese oxide, 20 per cent uranium oxide, and 125 per cent kieselguhr (based on the total weight of cobalt plus nickel). The activity of a cobalt-nickel catalyst promoted with the oxides of manganese, uranium, and thorium was found to be increased approximately ten per cent by a slow oxidation at 70° F. prior to its reduction.[21]

"Alloy-Skeleton" Catalysts

The heat-transfer problem involved in carrying out the highly-exothermic Fischer-Tropsch process over the poorly conductive, "conventionally" supported catalysts has prompted considerable investigation of catalysts which, by virtue of their finely-divided state or their physical structure, permit a more rapid distribution of the heat liberated during the reaction. Highly-porous, catalytically-active "skeleton" catalysts consisting of nickel or cobalt or alloys of both and possessing a greater coefficient of heat transfer than precipitated catalysts have been developed by Raney.[37, 82, 83, 85] These catalysts are prepared by alloying nickel and cobalt (singly or mixed) with aluminum or silicon and subsequently removing the latter material by solution in aqueous caustic. Experiments with cobalt-nickel skeleton catalysts have indicated that (1) the optimum ratio of cobalt to nickel is 1: 1, (2) catalysts prepared by alloying with silicon possess higher activity than those in whose preparation aluminum is used, and (3) the presence of even small amounts of copper or manganese in the catalyst is undesirable.[15] It has been shown that skeleton catalysts prepared from alloys of nickel with aluminum, nickel with silicon, nickel with manganese and silicon, and nickel with iron and aluminum are decidedly inferior to those prepared from nickel-cobalt-silicon alloys. The crystal structure of the catalyst obtained from a nickel-cobalt-magnesium alloy, upon microscopic investigation, has been found to be much coarser than that of the catalyst prepared from the corresponding silicon alloy.[48] The activity of skeleton catalysts prepared from nickel-aluminum, cobalt-aluminum, and cobalt-silicon alloys has been investigated by Rapoport and Polozhintseva,[39] and detailed studies of skeleton catalysts have been made by Japanese investigators,[31, 32, 47, 48, 49, 50, 51, 52, 53] who found that the yield of liquid hydrocarbons with such catalysts amounts to about 5.8 pounds per 1000 cubic feet of synthesis gas.

The preparation of catalyst pellets having an "integral, porous, metallic skeleton" has been described in U.S. Patent 2,136,509.[86] The method involved is somewhat different from that devised by Raney. The finely-divided oxide of a catalytic metal (e.g., nickel or iron oxide) is mixed with a finely divided metal (e.g., iron or copper), the mixture is compressed into pellets, and the pellets are heated in a reducing atmosphere at such temperature and for such time as is required to reduce most of the metal oxide to the catalytic metal and to cause alloying of the two metals, "the temperature and time of heating being insufficient to cause all of the catalytic metal of the oxide to alloy with the other metal and the temperature being

insufficient to cause sintering of the other metal in the absence of the catalytic metal."

Catalysts of the "alloy-skeleton" type deteriorate more rapidly and yield (at best) about 20 per cent less liquid product than precipitated catalysts having the same catalytic ingredients.[18, 22, 58] However, as mentioned, their ability to conduct heat more rapidly than precipitated catalysts has stimulated interest in their possibilities for the Fischer-Tropsch process.

Suspended Catalysts

The transfer of heat from the catalyst surface may also be facilitated by the use of finely-divided catalyst particles suspended in a liquid medium.[98] When the temperature of any given catalyst particle rises to a sufficient level, the excess heat from the reaction, instead of overheating the catalyst, is converted into heat of vaporization of the liquid. A catalyst consisting of iron, magnesium oxide, and zinc oxide suspended in anthracene oil is claimed to yield hydrocarbons heavier than gasoline (i.e., lubricating oil and paraffin wax) at temperatures below 700° F. and pressures above 300 pounds per square inch.[66] The use of a nickel-aluminum-kieselguhr catalyst suspended in a heavy, sulphur-free oil is said to result mainly in the production of methane.[80]

In one apparatus designed for the use of suspended catalysts, the catalyst is arranged in layers in a vertical tube, and a reflux condenser is provided at the upper end of the tube to return condensed fractions of the reaction product to the reaction zone, a substantial portion of this reflux consisting of oils which vaporize under the prevailing reaction conditions. The liquid medium is maintained at a level above the top layer of the catalyst, and the synthesis gas is introduced at the lower end of the tube. The catalyst (prepared by fusing a mixture of iron powder, silicon powder, titanium oxide, and potassium permanganate in a stream of oxygen (thereby converting the iron to magnetic iron oxide), cooling and comminuting the resulting mass, and treating the resulting particles with hydrogen is said to be suitable for the production of hydrocarbon oils boiling in the range of 105-570° F. at reaction conditions of 680-715° F. and 1470 pounds per square inch.[67, 87] Another technique involves introduction of the liquid medium into different zones of the reaction space.[75] The liquid medium may first be passed along the catalyst chamber "in indirect heat-exchange relation with the reaction participants and then through the chamber in the same direction as the reaction participants. Preferably, the liquid medium may be passed along the reaction chamber in countercurrent flow to the

reaction participants so that, while the liquid medium is at its lowest temperature, it comes into contact with the hottest part of the catalyst chamber, thereby keeping the temperature of the chamber much more uniform."[76] The liquid-phase catalytic synthesis has been discussed at some length by Fischer and Pichler.[16]

There are two main disadvantages of conducting the reaction in a liquid medium: (1) the difficulty of removing the reaction products and (2) the larger space requirements. Where the liquid medium is, itself, a fraction of the reaction product, the problem is less difficult than in the case where some other liquid is employed. Distillation or solvent extraction has been suggested for the latter case. Where the liquid medium differs markedly in chemical structure from the synthesis products; e.g., the medium is aromatic and products are paraffinic, highly selective solvents (such as sulphur dioxide) may be used.[66] The Standard Oil Development Company[71] has patented a process, designed to facilitate removal of the reaction products, in which the reaction is carried out in a 50-tray, bubble-cap tower with a catalyst suspension consisting of about three-quarters of a pound of finely-divided nickel catalyst activated with magnesium and aluminum oxides per gallon of sulphur-free paraffin wax. The yield is said to amount to about one gallon of liquid hydrocarbons per 1000 cubic feet of synthesis gas charged.

"Fluid" Catalysts

Perhaps the most recent development in the quest for a Fischer-Tropsch catalyst possessing superior heat transfer characteristics is the "fluidized" catalyst, which consists of very finely divided particles suspended in the synthesis gas stream. The experience gained in operation of the many (over 32) commercial-sized fluid catalyst cracking units[27, 42] already in operation should provide much of the "know how" for the analogous Fischer-Tropsch process.

Using such a catalyst for the Fischer-Tropsch process, it is claimed that the exothermic heat of reaction may be removed "immediately as it is formed along the path of the flowing gases in the reaction zone through the walls of the reaction zone by circulating a cooling medium without the walls of the reaction zone."[91]

In U.S. Patent 2,347,682,[93] which specifies this type of catalyst, it is said that the temperature can be kept substantially constant anywhere within the range of 225-425° F. by directly admixing relatively cool materials with the mixture in the synthesis zone. Unreacted gases and low-molecular-weight hydrocarbon gases are separated from the catalyst and recycled. Cool catalyst may be used to control the temperature of the reaction zone. A very recent patent[95] specifies

the circulation of a solid heat carrier through the reactor, along with the fluidized catalyst. The heat carrier must have a higher separating rate than the catalyst, in order to permit separation, cooling, and recirculation of the solid heat carrier.

The Standard Catalytic Company's "Chemican Process,"[94] a fluid-catalyst-type Fischer-Tropsch operation, maintains a pressure head at the bottom of the column containing the powdered catalyst by injecting an inert gas at one or more points. The pressure at the bottom of the column is said to be a direct function of the density of the catalyst powder and the height of the column. "Using 200-400 mesh activated clay having deposited thereon iron oxides, the pressure obtained was $\frac{1}{5}$ to $\frac{1}{8}$ pound per square inch per foot of column height. A minimum of 3-4 cubic feet of fluidizing gas (at conditions prevailing in the column) per 100 pounds of catalyst are required."

Supported Iron Catalysts

The ready availability of iron and its consequent low cost have long stimulated research on its use as a Fischer-Tropsch catalyst.[98, 99, 100] However, the effect of catalyst costs on the ultimate cost of Fischer-Tropsch products is said to be relatively slight in the case of modern commercial cobalt complex catalysts,[41] and perhaps the greatest present interest in iron catalysts centres around their ability to produce more unsaturated (hence higher-octane) gasoline fractions and the possibilities which they afford for utilizing water gas directly rather than after adjustment of the hydrogen-carbon monoxide ratio. An equimolar mixture of hydrogen and carbon monoxide is suitable for the synthesis over iron catalysts.[5]

Alkali-promoted iron-copper catalysts were used by Fischer and Tropsch in many of their early experiments.[17] However, they found these catalysts to be markedly inferior to cobalt or nickel catalysts, both in product yield and length of life.[11] The use of alkali, besides increasing the yield of primary product, is said to aid in the production of solid paraffin wax. Copper may be added to precipitated or impregnated iron catalysts to facilitate the reduction step in their preparation and to favour adsorption of the alkali salt.[11, 44] By using less copper in the catalyst, one pair of investigators [10] claimed to have obtained improved results, although others [25] found little, difference in the activities of catalysts with iron-copper ratios of 1:2 1:1, 3:1, and 5:1. The latter observed that catalysts containing 0.5 per cent alkali possessed longer lives than those containing greater proportions.

The promoting effect of alkali addition to iron catalysts is believed

to be the result of the formation (in its presence) of cubic ferric oxide (Fe_2O_3) and the prevention of its transition to the less active magnetic iron oxide (Fe_3O_4).[28] A number of X-ray diffraction and magnetic susceptibility studies have been made of such catalysts,[4, 5, 29] more recent investigations[46] having indicated that the inactive catalyst contains β-FeOOH and the active catalyst contains either α-FeOOH or α-Fe_2O_3 or both, but no β-FeOOH. It was found[46] that the highly-active catalysts had higher magnetic susceptibilities and were ferromagnetic, a suggested explanation being the possible presence of ferromagnetic alkali ferrites in the active catalyst.

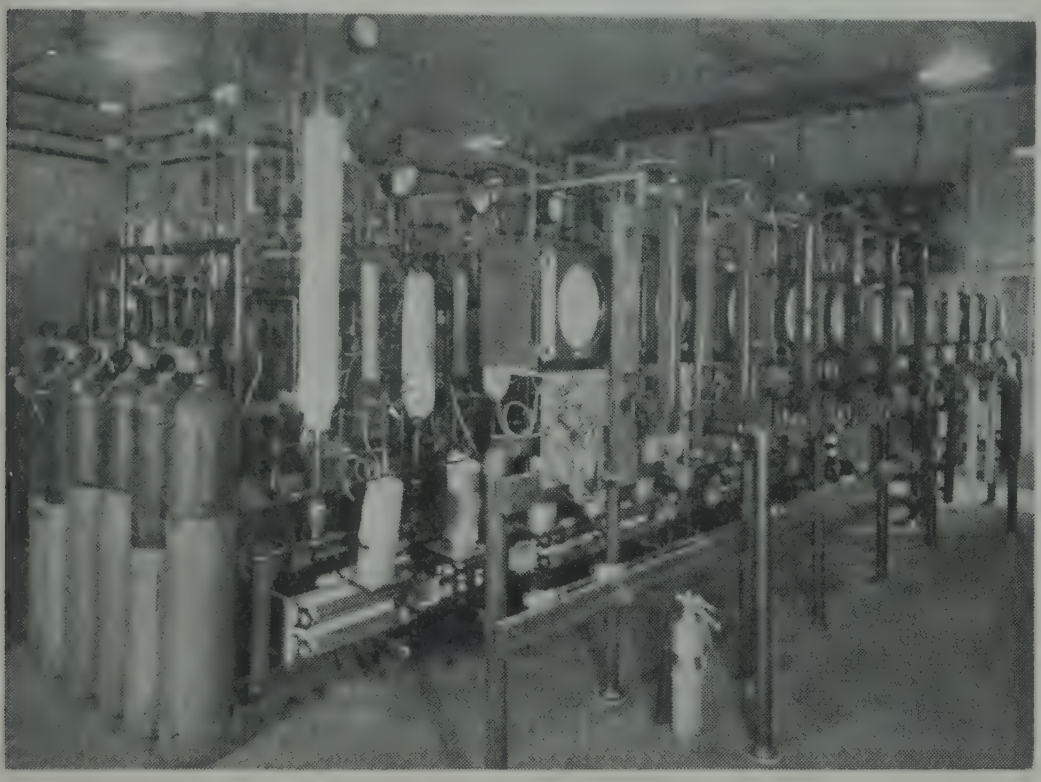

FIG. 8. *Catalyst testing units in Bureau of Mines Fischer-Tropsch laboratory, showing recording and indicating flowmeters.* (Courtesy of H. H. Storch, U.S. Bureau of Mines.)

The latest information emanating from the U.S. Bureau of Mines[20] indicates that catalysts prepared by the precipitation of a ferric salt with potassium carbonate or hydroxide are inactive if the original solution contains chloride anion and active if the original solution contains nitrate anion only. The difference in activity is very great; the catalysts precipitated in the presence of chloride ion produced from 2-3 grammes of liquid hydrocarbons per cubic metre of synthesis gas, while catalysts precipitated in the presence of nitrate ion

gave yields as high as 70 grammes. The active catalysts (precipitated from ferric nitrate) were found to contain α-Fe_2O_3, α-FeOOH, or both, while the inactive catalyst was found to contain β-FeOOH. The magnetic susceptibilities of the active catalysts were higher ($100\text{-}300 \times 10^{-6}$) than those of either α-Fe_2O_3 (25×10^{-6}), α-FeOOH (42×10^{-6}), or β-FeOOH (40×10^{-6}). The magnetic susceptibilities of the inactive catalysts (precipitated from ferric chloride) were quite close to the expected 40×10^{-6}.

Since both α-FeOOH and β-FeOOH decompose to α-Fe_2O_3 below 400° F., it is unlikely that the inactivity of the catalysts precipitated in the presence of chloride ion is caused by the presence of β-FeOOH, itself, but rather by some characteristic which its presence in the raw catalyst transmits to the ultimate (dried) catalyst. It may also be assumed that chloride ion is not directly responsible for the low activity of the catalysts, since active catalysts can be prepared from ferrous chloride, in which case no β-FeOOH can be formed.

Catalysts prepared by impregnating asbestos with the nitrates of the catalytic metals and small amounts of rare earth oxides have been found to give the following yields per 1000 cubic feet of synthesis gas: iron-copper-nickel (4 to 1 to 0.01), 1.8 pounds; iron-copper-nickel (4 to 1 to 0.02), 2.8 pounds; and iron-copper-nickel-cerium oxide-thorium oxide (4 to 1 to 0.05 to 0.001 to 0.006), 5.0 pounds.[19] Yields of 5.2 and 5.5 pounds per 1000 cubic feet of "water gas" ($1H_2$:1CO), respectively, were obtained with precipitated catalysts containing (in the first case) iron, copper, kieselguhr, and K_2CO_3 in the ratio of 4 to 1 to 5 to 0.08 and (in the second case) the same ingredients plus 0.08 part of manganese.[30, 55] The addition of five per cent of nickel or cobalt to these catalysts increased the yields when synthesis gas ($2H_2$: 1CO) was used, but proved undesirable for the gas containing equal amounts of hydrogen and carbon monoxide.

Sintered Iron Catalysts

Partial sintering of precipitated iron-alumina catalysts by reduction at about 1550° F. has been patented by I. G. Farbenindustrie A.-G.[68, 69, 72] This company also has patented catalysts of the iron group prepared by heating the corresponding metal carbonyl at a temperature above 930° F., but below the melting point of the metal, for such a period of time that partial sintering occurs.[70, 77, 78, 90] Earlier I. G. patents[63, 64, 65, 84] had specified the use of iron-group carbonyls in the synthesis under conditions which might possibly have caused some sintering.

In addition to use in the normal vapour-phase type of operation, such sintered iron catalysts may be employed in liquid-medium operations.[73, 88, 89] They also may be made in pellet form by mixing iron powder with an alkaline metal salt solution (such as aqueous potassium chloride), compressing, and reducing with hydrogen at about 1550° F.[74] Although single-pass yields are low, a satisfactory ultimate yield may be obtained by recycling the partially-spent synthesis gas.[92]

An I. G. Farbenindustrie report,[3, 5] written in 1939, concerns a rapid, hot-gas-recycle process over pelleted, sintered iron catalyst. The gas was passed through the reactor at hourly space velocities of 5,000-35,000, and the heat evolved in the synthesis was absorbed in an external heat exchanger. The reaction was conducted at 605-660° F. and 295 pounds per square inch. The conversion was about one per cent per pass, and about 1 per cent of fresh synthesis gas (0.9 H_2: 1 CO) was added per cycle, an equivalent amount of recycle gas being removed, freed of carbon dioxide, and sent to a second, smaller ($\frac{1}{4}$-size) recycle system. Conversion in the first stage was about 78 per cent and in the second stage about 13.5 per cent. The product was highly unsaturated, consisting mainly of gasoline of 85 Research octane number. A polymer gasoline of 97 octane number was made from the C_2-C_4 unsaturates. The yield of primary product was about 10 pounds per 1000 cubic feet of synthesis gas, of which approximately 0.87 pounds contained oxygenated compounds.

The hydrocarbons synthesized over sintered iron catalysts consist largely of branched-chain paraffins, while those produced on non-sintered iron catalysts contain very little iso-compounds. It is considered likely that sintering produces a critical spacing of the metal atoms in the iron carbide lattice which is conductive to the production of isoparaffins.[45]

Ruthenium Catalysts

Ruthenium or ruthenium-containing contact catalysts have been patented for the synthesis of solid hydrocarbons at temperatures of 300-540° F. and high pressures (over 450 pounds per square inch).[81, 98] Studies of other Group VIII metals (rhodium, palladium, osmium, iridium, and platinum) have shown that ruthenium is most satisfactory for this purpose.[83] The ruthenium catalyst is long-lived (no appreciable change in activity occurred during the one six-months test) and gives yields of approximately 6.2 pounds of paraffin wax and 3.1 pounds of liquid per 1000 cubic feet of synthesis gas at 380° F. and 1500 pounds per square inch.[13]

The effect of pressure upon the yield and type of products is very

pronounced. At atmospheric pressure, the yield is very low and the product consists of liquid hydrocarbons.[12] As the pressure is raised, the conversion at 355° F. increases rapidly until about 4400 pounds per square inch, then more slowly above this pressure, about 4.7 pounds of solid paraffin per 1000 cubic feet of synthesis gas being produced at 1300 pounds per square inch, 6.2 pounds at 4000 pounds per square inch, and 7.2 pounds at 4400 pounds per square inch.[35, 36] At all pressures, solid paraffins amount to about 60 per cent of the total yield of liquid and solid hydrocarbons, and gaseous hydrocarbons constitute 25 per cent of the over-all conversion. Fischer and Pichler [16, 35, 36] also studied the effect of pressure upon the synthesis over ruthenium catalysts, but they investigated only the range up to 1500 pounds per square inch.

The use of ruthenium catalysts for the commerical production of high-melting wax is not considered feasible by Dr Martin, director of Ruhrchemie A.-G., because of the relative scarcity of ruthenium. He has stated that hard wax can be produced more economically by using the conventional cobalt catalyst at low space velocities and low temperature.[5, 96]

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Chapter 8

REACTION VARIABLES

THE Fischer-Tropsch reaction takes place in a fairly narrow temperature range. Even with the most active nickel or cobalt catalysts, the reaction is very slow below 350° F. Above 440° F., with the same catalysts, the yield of liquid hydrocarbons diminishes rapidly, and methane yields increase correspondingly.[14] At higher temperatures (575-660° F.), methane production predominates, and the oxygen in the synthesis gas appears in the product as carbon dioxide rather than water. As mentioned, the optimum operating temperature with iron catalysts is higher than with nickel or iron, being about 465° F. However, the range in which satisfactory results are obtained is also quite small. The temperature coefficient of the synthesis on cobalt and iron catalysts is about 1.6 per 18° F. in the range of 370° to 445° F.[12] While the possibility of obtaining a given type of product depends to a large extent upon the catalysts and pressure employed, it is known that, in general, the hydrogenation of carbon monoxide produces straight-chain hydrocarbons at relatively low temperatures, alcohols in the range 575-750° F., isoparaffins in the range 750-885° F., and aromatics in the range 885-930° F.[2, 7]

Effect of Pressure

Generally speaking, the use of higher pressures in the Fischer-Tropsch process favours the formation of oxygenated compounds and hydrocarbons of high molecular weight, thus reducing the yield of liquid hydrocarbons.[3, 4] However, the use of medium pressures (75-220 pounds per square inch) has definite advantages, both in its effect on the total yield and upon the composition of the product.[17] Using a cobalt-thoria-kieselguhr catalyst without revivification over a period of one month, Fischer and Pichler[5] found that (1) the total yield increased with increasing pressures up to about 75 pounds per square inch, (2) the yield of paraffin wax increased with pressure up to about 220 pounds per square inch, and (3) the active life of the catalyst was greatest when medium pressures were used. Table II shows the results of their experiments over a pressure range of 0-2200 pounds per square inch. Martin[8] has reported similar results in two-stage operations.

TABLE II

Effect of Pressure on Yield and Type of Fischer-Tropsch Product[5]

Pressure, lbs. per sq. in. (Gauge)	*Yields, Pounds per* 1000 *Cubic Feet of Synthesis Gas* — *Total, Solid and Liquid*	*Paraffin Wax*	*Liquid above* 390° *F.*	*Gasoline below* 390° *F.*	*Hydrocarbon Gases,* C_1-C_4, *inclusive*
0	7.28	0.62	2.36	4.30	2.37
22	8.16	0.93	2.68	4.55	3.12
73.5	9.35	3.74	3.18	2.43	2.06
220	9.03	4.36	2.24	2.43	2.06
735	8.59	3.36	2.30	2.93	1.31
2200	6.48	1.68	2.12	2.68	1.93

At pressures of 75-220 pounds per square inch, the total yield of liquid and solid hydrocarbons obtained by Fischer and Pichler in the experiments just mentioned amounted to 9.35 pounds per 1000 cubic feet of synthesis gas when fresh catalyst was used, and still exceeded 6.24 pounds after 26 weeks of operation without catalyst revivification. On the other hand, at atmospheric pressure, the initial yield was 8.11 pounds and declined to 6.24 pounds after only one month of operation.[5] The effect of pressure on the synthesis over ruthenium catalysts has already been discussed.

The use of moderate pressures also offers the practical advantage of reduction in plant size for a given output.[10]

Effect of Throughput Rate

Using a cobalt-thoria-kieselguhr (100:18:100) catalyst in two-stage operation at a pressure of 150 pounds per square inch, Fischer and Pichler[6] found that both the yield of solid paraffin and the total yield of higher hydrocarbons decreased with increasing rate of throughput. At a throughput of 3.2 cubic feet per hour per pound of cobalt in the catalyst, they obtained yields of about 11.8 pounds of primary product per 1000 cubic feet of synthesis gas, of which 48 per cent consisted of solid paraffin; 44 per cent, liquid hydrocarbons; and 8 per cent, C_3-C_4 hydrocarbons. When the throughput was increased to 32 cubic feet per hour, 9.0 pounds of primary product were obtained, of which 14 per cent was solid paraffin, 73 per cent was liquid hydrocarbons, and 13 per cent was C_3-C_4 hydrocarbons. The necessity for utilizing higher reaction temperatures at increased throughput rates in order to maintain good yields leads to the formation of more methane. If the temperature is held constant, the yield drops rapidly with increased throughput rate, as may be seen from Table III, which shows the results obtained by using a cobalt catalyst at 390° F. and 220 pounds per square inch.

TABLE III

Effect of Increased Throughput on Yields at Constant Temperature [5]

Throughput (cu. ft./hr./lb./cobalt)	18.4	37.0	57.6	160
Total Yield (lbs./1000 cu. ft. syn. gas)	6.30	5.30	3.74	1.03

Similar data have been reported by Japanese[13] and British[1] investigators. Working at lower throughputs than those of Table III, Tsuneoka and Nishio[15] have observed that the yield rises to a maximum with increasing throughput before falling off. High space velocities favour the production of olefins.[11]

Generally speaking, "reducing the space velocity has an effect on the products similar to increasing the pressure, but with the important difference that a low space velocity reduces the output of the plant and a high pressure increases it."[10]

Effect of Hydrogen-Carbon Monoxide Ratio

As might be expected, increasing the relative amount of carbon monoxide to hydrogen in the synthesis gas results in the formation of a more olefinic product and the production of more carbon dioxide.[16] A high hydrogen-to-carbon monoxide ratio produces a saturated product and favours high methane formation. The amount of olefins in the reaction product has been found to be inversely proportional to the hydrogen content of the synthesis gas.[9] With conventional catalysts, a ratio of $2H_2$ to 1CO is considered optimum for obtaining the maximum total yields of hydrocarbons.[13]

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Chapter 9

GERMAN PROCESSES

THE reports of British Intelligence Objectives Sub-Committee (BIOS), Combined Intelligence Objectives Sub-Committee (CIOS), United States Technical Oil Mission (TOM) and Field Information Agency, Technical (FIAT) record Allied investigations of German technology made in the closing days of the war and for a time thereafter, and provide a fairly complete picture of the German process for the commercial-scale hydrogenation of carbon monoxide. Attention is especially drawn to two general reports [12, 16] which describe the commercial application of the process, and the research and development work which was in progress. The report[13] on the Fischer-Tropsch plants of Ruhrchemie A.-G. at Sterkrade-Holten is also of particular value, both because Sterkrade-Holten was an important research centre and because the plant served as a model for plants erected subsequently. A good general account of the operation and development of the process has appeared,[14] and the chemical engineering aspects have been admirably covered by Hall and Taylor.[15]

The German synthesis plants operated at temperatures of 355-390° F., either at atmospheric pressure or at medium pressures of about 150 pounds per square inch. The choice of atmospheric- or medium-pressure operation, in any given plant, was determined largely by the products desired. The medium-pressure synthesis is said to have given three times as much solid paraffin and about two months longer catalyst life periods than were obtained in normal-pressure operations. However, the synthesis at atmospheric pressure gave a higher gasoline yield. Martin (Ruhrchemie) believes that any post-war plants built in the predictable future should be of the medium-pressure type (because of the synthetic chemical possibilities), since the (German) synthetic gasoline (from coal) will not be able to compete with that made from petroleum, assuming normal peacetime conditions and a free world economy.[2]

The catalyst ovens used in the middle-pressure synthesis are interesting pieces of equipment, since they appear adaptable to almost any exothermic catalytic process carried out at constant temperature; e.g., the methanization of coke-oven gas.[1, 8] These ovens consist of groups of vertical tubes of two sizes, the smaller tubes being placed inside the large ones, concentrically. The catalyst

FIG. 9. *Section of Ruhrchemie A.-G. finned tube atmospheric pressure converter.* (Courtesy of H. H. Storch, U.S. Bureau of Mines.)

is placed in the annular space between the tubes. Temperature control during the exothermic reaction is maintained by passing steam through the inner tubes and the whole of the space between the outer tubes. Another type of medium-pressure reactor, the "Taschen-Rohr Ofen" (Chamber-Tube Oven), consists of single tubes containing a complex web of plates to facilitate the dissipation of heat.[1, 8]

The synthesis was carried out in two or three stages, with product recovery after each stage.[2] On the average, about 9.4 pounds of primary product were obtained per 1000 cubic feet of synthesis gas. The constituents of the primary product ranged from propane-propylene to waxes of molecular weights as high as 2000.[11] Generally speaking, the yield and quality of the products from the wartime synthesis did not differ materially from pre-war published information. Olefins of the C_3-C_4 fraction were converted to alcohols, etc., and residual paraffins were used as motor fuel. Low-boiling-range

gasoline of low octane number was used for blending in motor fuels. The middle fractions of high cetane number were used as Diesel fuel. The soft wax was largely converted into fatty acids for soap manufacture. Lubricating oils were synthesized from the heavy fractions.[2]

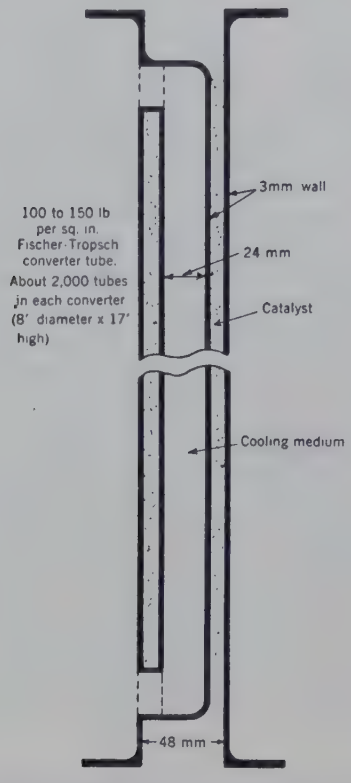
100 to 150 lb per sq. in. Fischer-Tropsch converter tube. About 2,000 tubes in each converter (8' diameter x 17' high)
3mm wall
24 mm
Catalyst
Cooling medium
48 mm

FIG. 10. *Section of Middle-Pressure Ruhrchemie Synthine reactor tube.* (Courtesy of H. H. Storch, U.S. Bureau of Mines.)

Considerable experimental work was done during the war on the development of recycle processes for the synthesis over commercial cobalt catalyst.[2] In contrast to the previously-mentioned rapid recycle process studies by I. G. Farbenindustrie for use with its sintered iron catalyst, these processes utilized a relatively low recycle ratio and the familiar, externally-cooled, middle-pressure reactor. On the pilot scale, Lurgi-Metalgesellschaft found it possible, at a recycle ratio of 3:1, to increase the throughput by 30 per cent without a sacrifice in yield or to realize a yield of about 10.6 pounds per 1000 cubic feet of synthesis gas at normal throughput. On the basis of pilot-plant performance, conversion of two commercial-scale plants to such operation was reportedly planned. Ruhrchemie A.-G., after similar experiments on the laboratory scale, installed recycle equipment in its Sterkrade plant, but this was destroyed by bombing before it could be put into operation.[2]

Iso-Synthesis Reaction

The conventional Fischer-Tropsch process, whether conducted at atmospheric or medium pressures, produces only small quantities of branched-chain hydrocarbons. The isobutane-iso-butylene content amounts only to about 10 per cent of the C_4 fraction with a cobalt catalyst and to about 15 per cent with an iron catalyst. The concentration of branched-chain compounds rises to approximately 20 per cent in the C_8 fraction with both catalysts, and the C_{16} fraction consists exclusively of isocompounds. However, the extent of branching seldom exceeds one methyl group on a long chain.[6, 7]

FIG. 11. *Inside of a single Ruhrchemie Synthine converter. Note the maze of tubes necessary for heat control in this type of equipment.* (Courtesy of W. C. Schroeder, U.S. Bureau of Mines.)

Although it has, as yet, been operated only on an experimental scale, the "Iso-Synthesis" process is of great interest since it offers means for producing high-octane gasoline (via alkylation) by a modified form of the Fischer-Tropsch process. It might be nearer the truth to say that the Iso-Synthesis is a modification of the Synthol process, rather than of the Fischer-Tropsch process, since it actually consists of first forming "higher" alcohols (mainly isobutanol), then dehydrating the alcohols to olefins, and finally hydrogenating the olefins to the corresponding isoparaffins. The process combines these three reactions in a single stage. By reacting synthesis gas containing

about 1 part hydrogen to 1.2 parts carbon monoxide over catalysts consisting of ZnO, Al_2O_3, ThO_2, or mixtures of one with another at temperatures of about 840° F. and pressures of about 4400 pounds per square inch, over 90 per cent concentrations of isoparaffins have been obtained in the C_4 and C_5 fractions of the reaction product.[3, 6, 7]

Research on the Iso-Synthesis reportedly was begun at the Kaiser Wilhelm Institut für Kohlenforschung in the fall of 1941,[6] and mention of it was made by Fischer[4] in 1943. However, no details were made public until after the investigation of the institute by the Allied Oil Mission.[7, 12, 16] According to Dr Helmut Pichler, the acting director of the institute, the catalysts suitable for the reaction include: (1) zinc oxide with alumina, (2) thoria alone, (3) thoria with alumina, (4) alumina alone, and (5) zinc oxide with thoria, cerium oxide, or zirconium oxide. The rate of throughput is five to ten times greater than that used in the conventional Fischer-Tropsch process. The yield of C_4 and higher hydrocarbons ranges from 3.74-6.85 pounds per 1000 cubic feet of the synthesis gas, depending upon the catalyst used. Typical product distribution in the C_4 and higher fraction is as follows:

C_4H_{10} (90 per cent isobutane) .....60-70 per cent by weight
C_5H_{12}(96-98 per cent isopentane .....20-30 per cent by weight
C_6-C_8 compounds ..... Small amounts

The C_6 fraction contains mainly 2-methylpentane and 3-methylpentane, but no neohexane or normal hexane. Some naphthenes have been found in the C_6-C_8 fraction. Larger quantities of hydrocarbons boiling above C_5 are obtained at lower reaction temperatures. About 0.62 pound of propane per 1000 cubic feet of synthesis gas is formed under the usual reaction conditions. In addition to the hydrocarbons produced, some alcohols, amounting to less than 10 per cent of the total hydrocarbon yield, appear in the reaction product. These alcohols consist primarily of isobutanol and a little methanol. The tail gas contains about 10 per cent methane (maximum), 30 per cent carbon dioxide, 20 per cent nitrogen, and 40 per cent carbon monoxide-hydrogen.

The temperature of operation is said to have a marked effect upon the reaction. At 750° F., alcohol production is high; at somewhat higher temperatures, dimethyl ether is formed; and around 840° F., isobutane is the major product. Raising the temperature still higher results in excessive carbon formation, and the catalyst requires frequent regeneration.

Carbon deposition puts a limitation on the size of the reaction tubes which may be used. Tubes of 12-15 millimetres (roughly half-inch) in diameter have proved satisfactory, while larger tubes have been found to encourage excessive formation of carbon.

Operation at pressures above 4400 pounds per square inch results in increasingly greater yields of oxygenated compounds. At 14,700 pounds per square inch, the principal product of the reaction is dimethyl ether. On the other hand, pressures below 4400 pounds per square inch result in smaller total yields.[3]

Aromatization Reaction

The Kaiser Wilhelm Institut was also engaged in the investigation of a process for producing aromatics by the hydrogenation of carbon monoxide.[2, 3, 4, 7, 10] Fischer [4] hinted at this work in 1943, and on-the-spot interrogation of Pichler [7] has supplied what details are known. The reaction is reportedly conducted over a catalyst consisting of an oxide of chromium, molybdenum, or thorium at a pressure of about 440 pounds per square inch and temperatures ranging from 885-930° F. About 5-10 per cent of potassium carbonate is included in the catalyst to reduce carbon formation. A 1 : 1 ratio of hydrogen to carbon monoxide is used.[2] The yield of liquid hydrocarbons is very small, usually below 0.62 pound per 1000 cubic feet of synthesis gas, but the product contains about 50 per cent aromatics (toluene and xylenes), the remainder consisting largely of naphthenes.[7, 10] The major portion of the synthesis gas is converted to methane and carbon. This synthesis was not considered very promising by the Germans.[3, 10]

Synthol Process

As mentioned in Chapter 1, an engineering concern [9] in the United States has recently announced that it is prepared to erect hydrocarbon synthesis plants which would use the "Synthol" process, developed as the outgrowth of original research and German data. No technical details were given, but it was mentioned that "this Synthol process ... under controlled conditions produces various chemical products in the form of oxygenated compounds." It was also stated, as is common knowledge, that "changing the operating conditions will control the quantity and quality of the production of the hydrocarbons and of the chemical compounds."

It has been noted that the German "Synthol" is a mixture of hydrocarbons and (chiefly) oxygenated compounds, produced by high-pressure synthesis, and that this use of high pressure materially reduces the liquid hydrocarbon yields.[5] Whether or not this new

"Synthol" process is similar in nature to its German namesake has not been revealed, but it would be no very difficult feat to produce hydrocarbon products from such a mixture as the German "Synthol," perhaps by hydrogenation or even by a reaction related to hydroforming.

As is evidenced by the commercial process for the production of synthetic methanol, oxygenated compounds can be produced in good yields by the hydrogenation of carbon monoxide over appropriate catalysts and under proper conditions (high pressures). Space does not permit a detailed analysis of these reactions here although they most certainly constitute part of the prior art of the Fischer-Tropsch process.[16]

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Part III

PRODUCTS AND BY-PRODUCTS

Chapter 10

PRODUCTS

AS HAS been pointed out, the catalytic hydrogenation of carbon monoxide can be made to yield a wide range of organic compounds, depending upon the choice of reaction conditions and the catalyst employed.[21, 22] From the synthesis of methane, by Sabatier and Senderens in 1902,[14] the successful production of higher hydrocarbons and their oxygenated derivatives by the Badische Anilin und Soda Fabrik in 1913,[20] and the early work of Fischer and Tropsch, dating from 1923,[6] techniques have been evolved which make possible (though not always economically feasible) the production of aliphatic hydrocarbons, alcohols, and other compounds, such as acids, ketones, esters, ethers, etc., of almost any chain length, degree of saturation, and (only recently) straight-chain, branched-chain, or cyclic structure.

Partly because the ordinary synthesis yields reaction products in which fuel-range hydrocarbons predominate, and partly because national programmes for self-sufficiency in petroleum have dictated such a course, widespread interest in the Fischer-Tropsch process has centred around its ability to produce gasoline, Diesel fuel, and lubricants. However, the synthetic chemical possibilities inherent in the process give it a significance much greater than that which it would possess if it produced only substitutes for petroleum. Thus, future developments may find the Fischer-Tropsch process being conducted primarily for one or more of the following purposes: (1) to produce maximum quantities of petroleum substitutes, with synthetic chemicals as by-products; (2) to yield large quantities of both petroleum substitutes and synthetic chemicals, neither class being relegated to by-product status; or (3) to produce mainly specialty synthetic chemicals, with fuels and lubricants in the role of by-products. The economic forces of supply and demand, in addition to the effect of changing technology, will dictate the future course of developments. Since Fischer-Tropsch economics and current developments will be discussed at some length in the last section of this book, it must suffice for the present to review the products obtainable from the synthesis and the processes by which the primary synthesis products may be converted into more valuable and useful materials.

Primary Products

The primary products of the normal (low pressure) Fischer-Tropsch process consist almost exclusively of straight-chain paraffinic and mono-olefinic hydrocarbons. Aromatics and naphthenes are ordinarily present in only negligible amounts. Depending upon the reaction conditions and the catalyst, the yield of oxygenated organic compounds may range from almost zero to several per cent.[5]

The hydrocarbons produced in the commercial, cobalt-catalyzed synthesis range from methane to hard waxes with average molecular weights of about 2000.[10, 16, 18, 19] With a ruthenium catalyst, products having molecular weights as high as 23,000 have been obtained.[13]

Depending upon the type of operation, somewhere between 10 to 15 per cent of the total product consists of methane. In the two-stage normal-pressure synthesis, the methane production amounts to 14 or 15 per cent. In the three-stage, medium-pressure process (150 pounds per square inch), the conversion to methane may be reduced by feeding a synthesis gas fairly low in hydrogen to the first stage and increasing the hydrogen-to-carbon monoxide ratio in the later stages. When this procedure is followed, the methane production may be reduced to about 10 per cent, with a consequent increase in the yield of higher hydrocarbons.[2, 4]

The "synthetic crude" obtained from the Fischer-Tropsch process is peculiar in one respect: it contains no fractions which possess good lubricant properties. This is not surprising, however, considering the lack of cyclic compounds, but it does necessitate further treatment of the products if a complete synthetic fuel-lubricants programme is desired. A number of methods for preparing synthetic lubricants from Fischer-Tropsch products are discussed in Chapter 15.

Product Distribution

Fischer-Tropsch "crude" from the atmospheric pressure synthesis consists of about 13 per cent liquefied petroleum gases (LPG), 52 per cent gasoline, 26 per cent Diesel oil, and nine per cent paraffin wax. Similarly, the primary product from medium-pressure operations contains approximately seven per cent LPG, 38 per cent gasoline, 30 per cent Diesel oil, and 25 per cent wax.[12, 21, 22]

Fischer[5] has stated that the optimum yield from the single-pass, atmospheric synthesis over cobalt catalyst is about 9.7 pounds of methane and heavier products per 1000 cubic feet of *ideal* synthesis gas. Table IV shows distribution of the fractions in the C_3-and-higher primary product.

TABLE IV

Product Distribution—Single-Pass, Atmospheric Synthesis [5]

Product	*Percentage by Weight of Total*	*Percentage Olefins by Volume*
C_3-C_4 fraction	8	55
C_5-300° F. fraction	46	45
300-390° F. fraction	14	25
390-600° F. fraction	22	10
Wax from oil	7	M. P. 120° F. (approx.)
Ceresin from catalyst	3	M. P. 190° F. (approx.)

The pre-war, German, two-stage commercial synthesis over cobalt catalyst is said to have resulted in the liquid product distribution shown in Table V.[16] Since the second stage of this process was operated at pressures above atmospheric (up to 150 pounds per square inch), a higher yield of wax was obtained than in Fischer's experiments at atmospheric pressure.

TABLE V

Primary Products from Pre-war Two-Stage Synthesis [16]

			Percentage by Weight —of Total—		*Percentage Olefins by —Volume—*	
Product	*Boiling Range*	*Specific Gravity*	*1st stage*	*2nd stage*	*1st stage*	*2nd stage*
C_3-C_4 fraction	—	—	5	2	50	25-30
C_5-300° F. fraction	85-300° F.*	0.66	26.5	8	35-40	20
300-575° F. fraction	200-575° F.*	0.74	26.5	11	12	12
Paraffin wax	—	0.85	—	21	—	—

* The overlapping boiling ranges of the liquid fractions resulted from the method of recovery; the lighter fraction was adsorbed on activated charcoal after condensation of the heavier fraction.

The "normal-pressure" (4 pounds per square inch), two-stage synthesis employed by many of the German plants during the late war yielded from 8.5 to 9.5 pounds of C_3 and higher hydrocarbons per 1000 cubic feet of ideal synthesis gas. As mentioned, methane constituted about 14-15 per cent of the conversion. Another 15 per cent of the total product consisted of the C_3-C_4 cut, of which approximately 49 per cent was propane, 16 per cent propylenes, 9 per cent butanes, and 26 per cent butylenes. Product distribution in the C_5 and higher fractions was as follows: 320° F. end-point gasoline, 50 per cent; 320-450° F. Diesel oil, 20 per cent; 450-600° F. heavy oil, 20 per cent; and wax, 10 per cent.[3, 16]

Operation of the Fischer-Tropsch process at medium pressures of about 150 pounds per square inch results in much higher wax yields and in smaller quantities of hydrocarbons in the gasoline boiling range. As mentioned, Ruhrchemie A.-G.'s director has stated preference for this process because valuable synthetic chemicals can be made from the wax.[2] Typical yields of primary products from three-stage operation of the medium-pressure synthesis are given in Table VI.

TABLE VI

Product Distribution—Three-Stage, Medium-Pressure Synthesis [2]

Product	*Percentage by Weight of Total*	*Percentage Olefins by Volume*
C_3-C_4 fraction	10	40 (13 per cent of C_4's are iso)
C_5-340° F. fraction	25	24 (about 45 O.N., MM)
340-535° F. fraction	30	9
535-640° F. fraction	20	Soft wax
Hard wax	15	M. P. about 195° F.

Much experimentation has been directed towards increasing the percentage of olefins in Fischer-Tropsch primary products. This work has been intended to serve the double purpose of increasing the octane number of the gasoline and of producing increased yields of unsaturates which are amenable to subsequent conversion operations such as the OXO process, polymerization, alkylation, and sulphuric acid absorption followed by hydrolysis to alcohols. For example, gas recycle over cobalt catalysts has been found to yield the following products:[2, 4]

	per cent	
C_3-C_4	8	(60-65 per cent olefins)
Gasoline	30	(60-65 per cent olefins)
Middle oil	28	(40-65 per cent olefins)
Wax	34	(small per cent of olefins)

Methods of increasing the olefin content of primary products have been discussed in some detail in the various chapters of Part II.

I. G. Farbenindustrie A.-G.'s hot-gas-recycle process over sintered iron catalyst, described in Chapter 7, is likewise designed to produce more valuable primary products.[1, 2] This process yields about 20 per cent methane (plus some ethane), 24 per cent C_2-C_4's, 38.5 per cent gasoline (7 per cent alcohols), 11 per cent gas oil (4 per cent alcohols), 1 per cent paraffin wax, and 5.5 per cent of alcohols which are dissolved in the reaction water. The C_2-C_4 cut contains about 8 per cent ethylene, 3 per cent propane, 9 per cent propylene, 2 per cent butane, and 8 per cent butylene. Moreover, 75 per cent of the C_4 fraction is said to consist of isobutane-isobutylene.[9]

By circulating a liquid fraction of the reaction product over a fixed bed of the same sintered iron catalyst (in order to remove the heat of reaction), the C_3-C_4 cut is said to amount to 16 per cent (85 per cent olefins); the gasoline fraction to 40 per cent (50 per cent olefins); the gas oil to 20 per cent (25 per cent olefins); paraffin wax

FIG. 12. *Charcoal absorption plant for Fischer-Tropsch gasoline recovery. Such plants were used extensively by the Germans.* (Courtesy of W. C. Schroeder, U.S. Bureau of Mines.)

to 20 per cent; and alcohols (mainly C_1 and C_2) to 4 per cent.[4] Interestingly enough, very similar yields are reported in reference 8, without mention of a liquid medium.

Product Recovery

In Germany at least, the C_3 and higher products of the synthesis are separated from the residual gas by first allowing the heavier products to condense and then recovering the lighter products by adsorption or absorption.

A common method in normal-pressure plants is to condense the heavier products (all but the light gasoline and C_3-C_4's) by direct contact with water in packed scrubbing towers, followed by adsorption of the light gasoline and C_3-C_4 hydrocarbons on activated charcoal.[3, 17] In a typical German, two-stage, normal-pressure

plant, each stage was equipped with a charcoal adsorption unit. Each unit consisted of seven towers, normally worked as follows: two towers adsorbing, one tower steaming, two towers drying, and two towers cooling. The time involved in each step was approximately as follows: adsorption, 40 minutes; steaming, 20 minutes; drying, 40 minutes; and cooling, 40 minutes.[3]

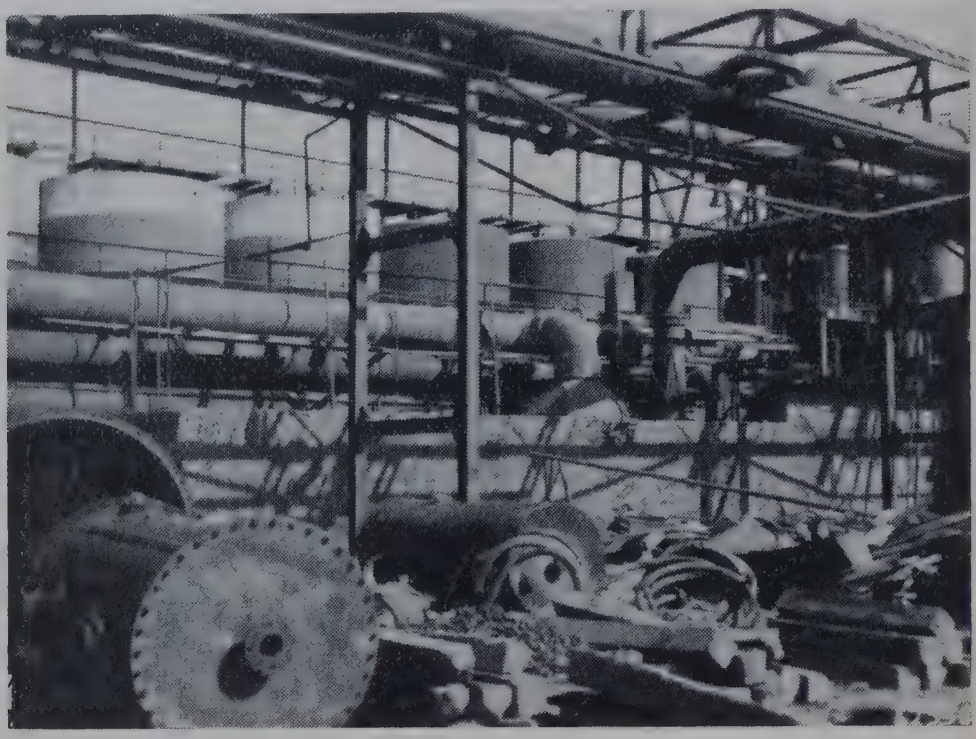

FIG. 13. *Charcoal absorption unit for gasolinerecovery from the product gases. Kamen Dortmund.* (Courtesy of W. C. Schroeder, U.S. Bureau of Mines.)

In the medium-pressure synthesis, the lighter products may be absorbed in oil, usually a fraction of the synthesis product.[17] Since only partial recovery of the C_3-C_4 fraction was attained, however, oil-scrubbing was not considered by the Germans to be highly satisfactory.[7] The more common procedure involved the use of activated carbon at atmospheric pressure. The Linde organization reportedly advocated recovery of all products, including the C_3-C_4 fraction, by cooling under pressure; however, it was stated that this had not been tried commercially.[7]

The carbon dioxide content of the gas which remained after removal of the C_3 and higher products was reduced by use of the Alkazid process.[7] As mentioned in Chapter 5, this process, which involves the use of an alkaline organic compound, was used in some German Fischer-Tropsch plants to remove hydrogen sulphide from the synthesis gas.[2, 11 15,]

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Chapter 11

GASEOUS FUELS

AFTER recovery of the C_3 and higher products, the residual gas from the Fischer-Tropsch process consists mainly of methane, unconverted synthesis gas, carbon dioxide, and nitrogen, and also contains small amounts of ethane and ethylene. The relative proportions of these individual gases vary considerably with the type of operation and the reaction conditions. In one plant, the residual gas from the two-stage, normal-pressure synthesis was found to contain 30.9 per cent methane, 18.0 per cent hydrogen, 10.5 per cent carbon monoxide, 20.3 per cent carbon dioxide, 18.5 per cent nitrogen, and 1.6 per cent ethane-ethylene. The heating value of this gas was about 395-425 B.Th.U. per cubic foot. In some plants, part of the dry gas from the charcoal adsorption step was returned to a coke-oven-gas cracker for reconversion of its methane content to synthesis gas, while the balance was burned as a lean fuel gas.[1] In others, the entire gas was simply used as fuel for heating in such other plant operations as gas production and purification.[1]

The fact that from 10 to 15 per cent of the synthesis gas is converted to methane in the Fischer-Tropsch process makes it advisable, from the economic point of view, to utilize the methane thus produced for as thermally useful a purpose as is possible. The "upgrading" of manufactured gas is one such use; in fact the gas works of the city of Leipzig, Germany, was installing a Fischer-Tropsch plant with this purpose in mind when the war ended.[5] This plant, which produced 5,826,150 cubic feet of coke-oven gas and 8,121,300 cubic feet of water gas per day, planned to mix 2,612,940 cubic feet of the coke-oven gas and 5,155,260 cubic feet of the water gas to make 7,768,200 cubic feet of synthesis gas, which was then to be fed to the Fischer-Tropsch plant. In addition to the highly-desired liquid and solid Fischer-Tropsch products, about 3,884,100 cubic feet of residual gas would have been obtained, which, when mixed with the 3,213,210 cubic feet of coke-oven gas and 2,966,040 cubic feet of water gas, which were not to be utilized for synthesis gas, would have supplied the city with 10,063,350 cubic feet per day of gas having a heating value of about 450 B.Th.U. per cubic foot and a density of 0.0394 pound per cubic foot. The percentage compositions of the gases mixed and the composition of the finished city gas may be seen in Table VII.

TABLE VII

Upgrading Manufactured Gas with Fischer-Tropsch Residual Gas [5]

Analysis, Vol. %	*Coke-Oven Gas* (3,213,210 *cu. ft./D*)	*Water Gas* (2,966,040 *cu. ft./D*)	*Residual Gas* (3,884,100 *cu. ft./D*)	*Resultant City Gas* (10,063,350 *cu. ft./D*)
CO_2	2.4	5.0	8.1	5.4
C_nH_m	1.2	—	1.0	0.8
O_2	0.4	—	—	0.1
CO	5.7	38.0	21.3	21.2
H_2	59.0	52.0	37.5	48.6
CH_4	27.8	0.3	23.6	18.1
N_2	3.5	4.7	8.5	5.8

Methane Synthesis

Considerable interest has been evidenced in Britain[10, 11] and America[6] in the direct production of methane from carbon monoxide and hydrogen, although this is a reaction usually minimized in every possible way during the normal Fischer-Tropsch process. "Synthetic natural gas" has a much more desirable calorific value than the water gas from which it is produced, so that this phase of the Fischer-Tropsch process constitutes a "gas-upgrading" method. Similarly, the other hydrocarbon gases produced to a greater or lesser extent—ethane through the butanes—are desirable fuel gases themselves or may be used for gas enrichment. A process for increasing the calorific value of coal gas used as road transport fuel was developed in Germany.[12]

Gerdes[3] has given this matter some attention in an article published in 1941, and a recent British article[2] has also dealt with the subject in some detail. Reference should also be made to Chapter 6 for a discussion on the reaction mechanism; where methane is desired as the primary product, every effort is made to avoid polymerization of the (CH_2) groups which form on the hydrogenating catalyst. Logically, nickel is the basic material of most of the catalysts investigated.

Komarewsky and Riesz[6] have reported that "the conditions favouring the production of methane rather than Fischer-Tropsch synthesis of higher-molecular-weight hydrocarbons are: (1) catalyst, (2) relatively high temperature, and (3) high proportion of hydrogen in the reacting gas. Nickel and iron are active at atmospheric pressure. The temperature required is about 570° F. for nickel catalysts. The ratio of hydrogen to carbon monoxide theoretically should be three ($CO + 3H_2 \rightarrow CH_4 + H_2O$)." Even carbon dioxide can be hydrogenated to methane under certain conditions.

The C_3-C_4 Fraction

The C_3-C_4 fraction generally constitutes about 13 per cent of the crude liquid product obtained from the normal-pressure synthesis and about 7 per cent of that produced in medium-pressure operation.[8] This fraction is of special interest in any consideration of the Fischer-Tropsch process because of the prospects it offers for the manufacture of high-octane polymer or alkylate gasolines. Synthetic alcohols may also be produced from the olefins by sulphuric acid absorption and subsequent hydrolysis or by the OXO process.[9] The propane and normal butane naturally possess value as LPG fuels. However, since both economics and wartime demands favour production of hydrocarbons more readily adaptable to further synthesis, much effort has been devoted towards producing greater quantities of olefins and isocompounds in this fraction.

Methods of raising the olefin content have already been discussed, and the "Iso-Synthesis" process was treated in Chapter 9; it is obvious that the quantities of alkylate and/or polymer gasoline obtainable from the Fischer-Tropsch process are functions of the isobutane-isobutylene and the olefin content of this fraction.

It may be of interest to review here some of the uses to which the Germans have put the C_3-C_4's produced in their commercial processes. In some of the commercial plants, the C_3-C_4 cut was absorbed in sulphuric acid and hydrolyzed to alcohols, some incidental polymer being also formed and used for blending in motor fuel. In one typical, normal-pressure plant, this fraction was contacted for about one hour with 58° Baumé sulphuric acid at about 110° F. and 150-220 pounds per square inch. After a 30-minute settling period, the ester-acid bottom layer was drawn off and contacted with water at atmospheric temperature and pressure. This caused separation into a relatively small upper layer of polymer and a larger lower layer of ester. The ester layer was hydrolyzed in a four-stage system by heating with open steam at an absolute pressure of about 3 pounds per square inch. The temperatures in the successive stages were as follows: Stage 1, 160-175° F.; Stage 2, 175-190° F.; Stage 3, 190-203° F.; and Stage 4, 203-220° F. The hydrolized product contained alcohols in about 50 per cent concentration, while the acid was reduced to about 25 per cent H_2SO_4. The upper layer removed from the primary (sulphuric acid) contactor contained the paraffinic C_3-C_4's and some polymer. All products were caustic washed, the polymer from both the upper and lower primary layers was blended in motor fuel, and the unreacted (paraffinic) C_3-C_4 fraction was compressed for use as bottled-gas motor fuel. From 26-28 tons per day of C_3-C_4 fraction (about 30 per cent olefins),

about 2.0-2.1 tons of isopropyl alcohol and 3.2-3.5 tons of mixed secondary- and tertiary-butyl alcohols were produced.[1]

The Treibstoff Werke Rheinpreussen at Moers (near Duisberg) is said to have produced approximately 2600 tons of mixed C_3-C_4 alcohols during 1943 by the sulphuric acid method. Acid of about 75 per cent strength was employed at temperatures up to 140° F. Isopropyl alcohol accounted for about 99 per cent of the propylene treated, and secondary butyl alcohol made up about 90 per cent of the products from butylene. Approximately 5 per cent of the total product consisted of ethers.[7]

The Germans do not appear to have put very strong emphasis on the production of polymer gasoline or alkylate from Fischer-Tropsch C_3-C_4's, although they were somewhat active along this line. Evidently the strong demand for C_3-C_4 alcohols and the fact that coal hydrogenation was strongly favoured (politically) for gasoline production both served to de-emphasize this development. However, research on the "Iso-Synthesis" was continued throughout the war, and polymer plants had been built. The Castrop-Rauxel plant of Klocknerwerke A.-G., for example, was found to possess a polymer gasoline unit capable of processing 25 tons of C_3-C_4 fraction per day at about 2950 pounds per square inch by the phosphoric acid process. On the basis of 10 days of experimental runs, a 45 per cent yield of polymer gasoline was expected.[4]

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Chapter 12

GASOLINE

GASOLINE from the conventional Fischer-Tropsch process is notoriously low in octane number as a result of its straight-chain, paraffinic structure. Consequently, these gasolines are usually cut to a low endpoint to maximize, as far as possible, the effect of the higher-octane lower ends. The C_5-300° F. fraction of Fischer's atmospheric synthesis (see Table IV), despite its 45 volume per cent of olefins, tested only about 55 octane by the Motor Method.[8] The lead susceptibility, however, was high, 0.5 cubic centimetres of tetraethyl lead raising the rating to 72 octane.

Ruhrchemie's pre-war, two-stage process yielded an 85-285° F. gasoline of 62 octane number or an 85-230° F. gasoline of 67 octane.[16] Such gasoline was, of course, too volatile for ordinary use, and the low cut point greatly reduced the gasoline yield. In order to convert the higher boiling fractions into usable gasoline, the company turned to thermal cracking, installing True-Vapour-Phase cracking units at two of its plants.[16] The choice of the True-Vapour-Phase process was said to have been made after "exhaustive tests" of the merits of various thermal cracking processes in the treatment of Fischer-Tropsch products. The conditions of cycle-gas circulation in the T-V-P process favour polymerization of light olefins, a fact which was recognized as affording a means of converting the C_3-C_4 cut of the Fischer-Tropsch product to polymer gasoline, thus increasing both the yield and the octane number of the finished gasoline.

Table VIII shows the results of cracking Fischer-Tropsch "crude",

TABLE VIII

T-V-P Cracking of Fischer-Tropsch Crude Oil [16]

Charge Stock	*Reduced Crude*			*Untopped Crude*	
Specific Gravity	0.769			0.725	
Cracked gasoline:					
Yield, % by weight	81	75.5	65.2	70.6	65.2
Yield, % by volume	88	81.8	73	72	68.3
Specific gravity	0.7079	0.7096	0.6876	0.7114	0.6920
End Point, °F.	392	386	333	386	320
Octane number, MM*	62	68	75	67	73
TEL** to raise to 80 O.N., c.c./gal.	—	3.5	1.3	3.7	1.7

* MM = motor method.
** TEL = tetraethyl lead.

while Table IX gives data on the yields and quality of gasolines prepared by cracking the heavier fractions of the crude and blending with the light gasoline fraction collected by charcoal adsorption.

TABLE IX

Yield of Cracked and Blended (380° F.E.P.) Fischer-Tropsch Gasoline [16]

Per Cent by Weight of Total Liquid Products	*Run* 1	*Run* 2	*Run* 3
Before Cracking			
Charcoal-adsorbed gasoline (unstabilized)	42.5	40	30
Cracking stock	57.5	60	70
Total primary product	100	100	100
After Cracking			
Charcoal-adsorbed gasoline (stabilized)	40	37.5	28
Cracked gasoline (stabilized)	44	44.5	47
Total blended gasoline	84	82.0	75
Octane number (MM)* of finished blend	63	68	70

* MM = motor method

In early 1938, Ruhrchemie was not utilizing its cracking plants to upgrade Fischer-Tropsch gasoline as just mentioned, but was instead blending low-octane synthetic gasoline with benzole and alcohol in accordance with the then-existing German motor fuel regulations.[16] Martin [14] and Davies [6] have also described Ruhrchemie's thermal cracking installations.

A "Carburol" cracking plant was erected at the Moers plant of Steinkohlen-Bergwerk Rheinpreussen, but it is said that it never was used to crack the Fischer-Tropsch oils, presumably because they were considered more valuable as Diesel fuel than as cracking stock.[1]

Starting with a liquid Fischer-Tropsch product boiling between 113° F. and 702° F., Egloff, Nelson, and Morrell [7] obtained 84 volume per cent (based on charge) of 66-octane-number gasoline by subjecting the entire fraction to distillation, thermally reforming the naphtha, thermally cracking the bottoms, and catalytically polymerizing the cracked gases. The yields from the various steps are shown in Table X. The octane number of the gasoline and the yield based on synthesis gas charged could, of course, be raised somewhat by also polymerizing the C_3-C_4 fraction of the Fischer-Tropsch product.

TABLE X

Processing Fischer-Tropsch Liquid Product [7]

Product	*Yield, Vol. % on Charge*
Light gasoline (cut at 97-241° F., 68 O.N.)*	29.1
Reformed gasoline (from 219-523° F. naphtha)**	26.8
Cracked gasoline (from bottoms)	22.6
Polymer gasoline (from cracked gases)	5.8
	84.3

* O.N. octane number.
** Octane number of naphtha fraction before reforming was 4.

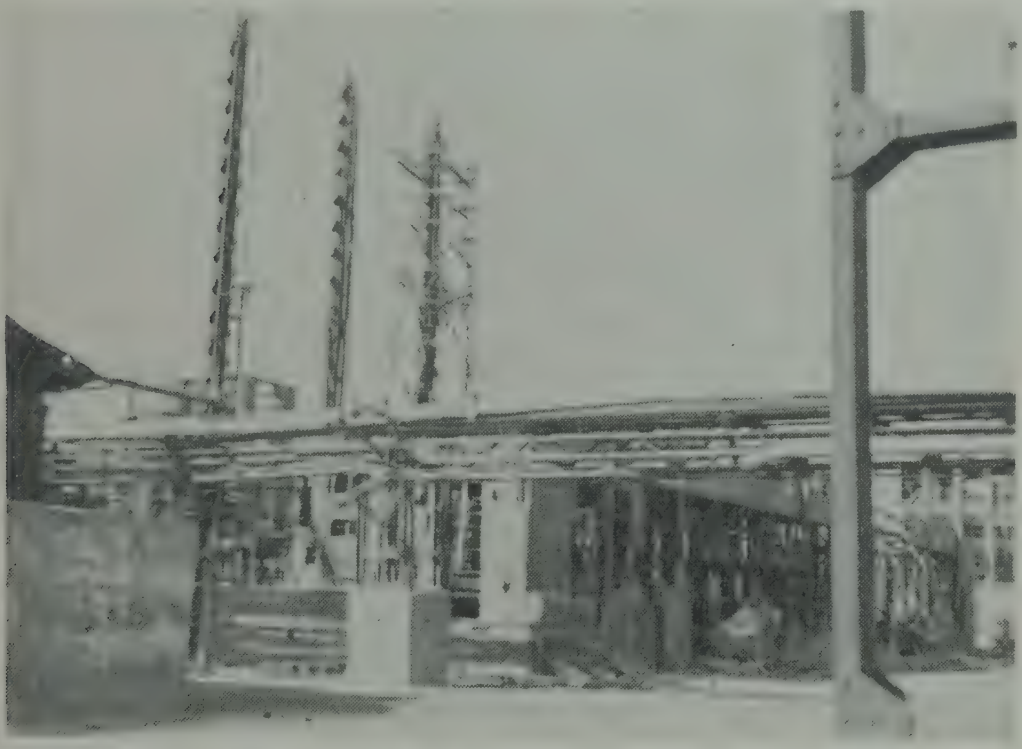

FIG. 14. *Ruhrchemie cracking plant for Fischer-Tropsch products.* (Courtesy of W. C. Schroeder, U.S. Bureau of Mines.)

According to Velde,[19] Ruhrchemie later developed a catalytic reforming process in which the gasoline fraction was passed in the vapour phase over a special (unidentified) catalyst at a temperature somewhat below that at which appreciable cracking would take place. The vapours from this step were then cooled and passed over the same catalyst at a lower temperature. Increases of 8-24 points in octane number were claimed for the process. It was believed that this improvement was the result of an isomerization of the charge

which included both branching and a shift in the position of the double bonds within the olefins, displacing them from the ends of the molecule to positions nearer the middle and thereby increasing the anti-knock rating.[10] Illustrative of the effect of olefin content on the reforming ability of the process was the treatment of a gasoline of 44 octane number which contained 35 per cent olefins; this was upgraded to 52 octane, while another gasoline of 41 octane number, containing 55 per cent olefins, was raised to 61 octane by similar treatment.

Fischer and Weinrotter [9] have cracked Fischer-Tropsch heavy oils with electrically-heated, platinum-wire spirals at lowglow temperatures. Over 50 per cent of the oils can thus be cracked, with up to 90 per cent of the cracked product consisting of unsaturated hydrocarbons. A number of references to similar earlier work of Fischer and his co-workers are given by these authors.

Russian investigators [2] have experimented with the aluminum chloride cracking of fractions of the Fischer-Tropsch products. The products boiling above 470° F. and including the solid fraction require the use of approximately 20 per cent of aluminum chloride for good cracking results. The solid fraction, boiling above 570° F., is said to require only 10 per cent of aluminum chloride for satisfactory results. Maximum yields, however, are claimed for 15 per cent aluminum chloride, about 48 per cent gasoline thus being produced. The 70-300° F. gasoline is said to be composed almost exclusively of isoparaffins. The octane number of the 70-122° F. fraction, which contains C_5's and C_6's, is said to be about 88; that of the 122-212° F. fraction, 73; and the rating of the entire gasoline cut, 79.

Kingman and Cawley [13] have recently reported the results of experiments on both thermal and catalytic cracking of a 390-570° F. Fischer-Tropsch middle oil. In order to determine the yield of light hydrocarbons obtainable by thermal cracking with recycle, a series of runs were made at 1175° F., from each of which, the product boiling above 390° F. was separated and used as charge for the succeeding run. Except for a slight decrease in the yield of gas, there was little difference between the yields from the original oil and those from the recycled oils, as may be seen from Table XI.

Recycling of the cracked product boiling above 390° F. resulted in a total yield of 37.8 per cent of gasoline to 390° F. and a gas yield of 6.4 cubic feet per pound of charge. The thermally cracked gasoline boiling up to 390° F. had a bromine number of 130, while the fraction up to 337° F. had a bromine number of 148 and contained approximately 80-90 per cent of olefins and less than 2 per cent of aromatics.

From thermal cracking runs made at 1040° F., 1110° F., and 1175° F., it was observed that the gaseous products obtained at all three temperatures contained less than three per cent of hydrogen and approximately 60 per cent of olefins. When the cracking temperature was increased from 1040 to 1175° F., the olefin content of the gas rose from 57 to 63 per cent. Butadiene production was small but increased appreciably with rises in cracking temperature. The paraffinic gases consisted mainly of methane and ethane, and the olefins were chiefly ethylene and propylene with a lesser amount of butylene.

TABLE XI

Simulated Recycle Thermal Cracking of Fischer-Tropsch Middle Oil [13]

Charge Stock	*Run Number*	*Liquid Product, % by weight of charge*	*Gas Yield, cu. ft./lb. charge*
Raw middle oil	1	67.5	3.53
Raw middle oil	2	67.7	3.40
Residue over 390° F. from Runs 1 and 2	3	70.0	3.21
Residue over 390° F. from runs 1 and 2	4	68.0	3.34
Residue over 390° F. from Runs 3 and 4	5	70.0	3.22

These catalytic cracking experiments showed that cracking in the presence of a mixed silica-alumina catalyst at 1110° F. results in an increase in the gas yield and a pronounced change in the composition of the products, the gasoline containing a smaller proportion of olefins and more aromatics and saturated compounds. "The use of the catalyst also increased the proportion of hydrogen, reduced the proportion of paraffins in the gas and, although not greatly changing the proportion of total olefins, favoured the production of propylene and butylene in place of ethylene, and completely suppressed the formation of butadiene. Evidently the catalyst influenced the cracking of carbon-hydrogen bonds as well as carbon-carbon bonds."[13]

Sergienko [15] has reported experiments on the cyclization of the heptane-octane and the nonane fractions of Fischer-Tropsch products. These experiments were carried out at about 885° F. over alumina-chromia-cobalt oxide or chromia-cobalt oxide catalysts. Aromatics constituted more than 50 per cent of the product, while cracked products amounted to about 5-10 per cent and aliphatic unsaturates to about 4-12 per cent.

According to Director Martin, Ruhrchemie was constructing a

catalytic cracking plant to produce C_3-C_5 olefins from C_7 and higher Fischer-Tropsch fractions. These olefins were to be used to make polymer gasoline. Pilot-plant tests indicated that the "Granosil" catalyst (acid-treated clay) would have a life of 6-8 weeks, after which it would be discarded. During use, the catalyst required carbon removal (by oxidation) at intervals of 8 to 10 hours. This catalytic cracker was about 60 per cent complete when construction was abandoned in mid-1944.[10]

As mentioned, the raw gasoline fraction from the I. G. Farbenindustrie's hot-gas-recycle process over sintered iron catalysts contains about 7 per cent of alcohols. In the raw state, this fraction has an octane number of 68-70 by the Research Method. Passage of this gasoline over alumina at 750-840° F. for dehydration of the oxygenated compounds, followed by refining over fuller's earth at 355-390° F., raises its rating to about 84 octane by the Research Method and 75-78 octane by the Motor Method. The refined gasoline is said to contain about 70 per cent olefins.[3] This gasoline appears to be somewhat similar to that produced by the Hydrocol process, which apparently is a fluid catalyst process using "cheap, rugged, iron catalysts. ... The finished gasoline produced by Hydrocol with a Reid vapour pressure of 10 pounds has a clear octane number of 80 Motor Method or 88-90 Research."[12]

Since the synthesis gas is (at present) made as nearly sulphur-free as possible prior to the synthesis reaction, and since practically no diolefins are formed in the synthesis, raw Fischer-Tropsch gasoline normally requires neither desulphurization nor treatment to improve its gum stability. The only treatment needed (short of octane number improvement) is a light alkaline wash to remove organic acids.[18]

According to Dannefelser,[5] practically no gum formation takes place during prolonged storage of Fischer-Tropsch gasoline, and the mono-olefin content (30-40 per cent in his samples) remains unchanged. When the gasoline is stored in large batches, peroxide formation is said to be negligible. However, the octane number of a small sample stored for 15 months in a sealed can was lowered by three units. Ortho-cresol has been suggested as a peroxide inhibitor.

An interesting method for predicting the octane number of stabilized Fischer-Tropsch gasoline from its "olefin index" and "vaporizability" has been advanced by Hammerich.[11] For raw Fischer-Tropsch gasoline, the determination has been said to deviate by less than one octane number from the rating experimentally obtained by the CFR Research Method. However, any treatment of the gasoline, such as reforming or blending with other fuels, invalidates the relationship.

Tannenberger and Seifert [17] have reported that the method of R. B. Cox [4] for calculation of the octane number from density and boiling range gives values within at least two numbers of the experimentally determined rating when applied to Fischer-Tropsch gasolines.

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Chapter 13

DIESEL OIL

FISCHER-TROPSCH fractions of the Diesel oil boiling range usually possess exceptionally high cetane numbers. In fact, in the conventional, cobalt-catalyzed synthesis, cetane numbers of 100 or more have been obtained. A typical Diesel oil fraction might boil from 390-680° F. and have a specific gravity of about 0.769, a hydrogen content of 15.2 per cent, and a heat of combustion of 18,900 to 20,300 B.Th.U. per pound.[8] Synthesis procedures which are designed to produce more olefins naturally yield Diesel fractions of lower cetane number; however, even these fractions have higher cetane numbers than are common in Diesel fuels from other sources.

The Fischer-Tropsch fraction actually used for Diesel fuel by the Germans during the war had a much lower boiling range than that just mentioned. Their "SDK" fuel had a boiling range of 310-485° F., a density of 0.743-0.749, a solid point of −36 to −42° F., and a flame point of 80-120° F. This fuel, which had a cetane number of 75-78, is believed to have consisted entirely of a Fischer-Tropsch fraction with (probably) a pour-point depressant added.[1]

The motivation behind the German use of such low-boiling fractions for Diesel fuel is not entirely clear from the available information. However, there appear to have been several significant factors involved in such use. As mentioned, Fischer-Tropsch gasoline was cut to a low end point to attain as high an octane number as possible. The strong demand for Diesel fuel (and possible lack of octane-improving facilities) prompted them to add the heavier gasoline to the Diesel fraction, thus lowering the latter's initial boiling point. The Diesel fuel was made even lighter by appropriation of the heavier oils for conversion to "Mersol" detergents.[4] It has also been indicated that straight Fischer-Tropsch fractions, in spite of their high cetane numbers, do not make the most satisfactory Diesel fuels and that blending Fischer-Tropsch fractions with petroleum oils or oils obtained by coal distillation or hydrogenation yields fuels of superior combustion characteristics.[2]

Some amplication of this last point might be desirable here. A recently published article[7] has reported the results of combustion studies on a series of fuels of narrow distillation range and 40-90 cetane number. The paraffinic, high-cetane fuels were found to produce more black smoke (indicative of fuel waste) and to exhibit a

lower rate of pressure rise and a lower peak cylinder pressure during combustion. It is believed that highly paraffinic fuels, being less refractory cracking stocks, may be more susceptible to pyrolysis in the combustion chamber, producing more carbon, some of which emerges from the exhaust as black smoke. The low rate of pressure rise with Fischer-Tropsch Diesel fuel may be raised by blending it with aromatic fuels (such as tar oils) which possess characteristically high rates of pressure rise.[9]

Competitive tests with a high-cetane Fischer-Tropsch fraction and a 47-cetane petroleum cut showed that use of the Fischer-Tropsch fraction entailed an increase in fuel consumption of about 5 per cent (based on equal heat value) and an increase in exhaust gas temperature of some 25 per cent.[2]

Blending of Fischer-Tropsch product with low-cetane fuels from other sources, then, both improves the combustion characteristics of the former and the cetane (ignition characteristic) of the latter. Typical German blends are said to have contained 40-45 per cent of Fischer-Tropsch fraction and 55-60 per cent of either a petroleum gas oil or a fraction produced by distillation or hydrogenation of coal. These blends, however, contained asphalt gum and carbon-forming materials which tended to clog engine injection systems, and various processes had to be developed to refine them. One method consisted of treatment with gaseous sulphur dioxide at atmospheric pressure. This process is said to have been inexpensive, since the sulphur dioxide was recirculated, and makeup was small.[1, 2] Kolbel [6] has discussed the blending of Fischer-Tropsch product with oils obtained from coal by hydrogenation, distillation and extraction. He has claimed that mixtures containing 40-55 per cent Fischer-Tropsch oil possess cetane numbers of 65-85 and compare favourably with petroleum fuels in ignitability, resistance to carbon formation, and completeness of combustion. Table XII compares the inspections of a Fischer-Tropsch fraction, a tar oil fraction (from coal distillation), a blend of the two, and a typical petroleum gas oil.

The process by which the heavier Diesel oil fraction (445-605° F.) was converted to synthetic detergents is discussed in a later chapter. However, it might be pointed out that Martin (Ruhrchemie) considered such chemical developments as the logical future use of the Fischer-Tropsch process (for Germany, at least) and felt that its use for fuel production was economically unsound, in spite of the premium Diesel fuels it can provide.[3] The fact that such chemical production was conducted during the war, when Diesel fuels were in critical demand, may illustrate his point, although such an assumption should be examined in the light of other factors; namely, that

soap and detergent supplies were likewise extremely short and that Nazi party politics (reportedly) influenced the German fuel policy in favour of coal hydrogenation over the Fischer-Tropsch process.

It is interesting to note [5] that the Diesel oil to be produced in the United States at the proposed Brownsville, Texas, plant of Carthage Hydrocol, Inc., will have "a gravity of about 38° API, a cetane number of 45-50, and a pour point below 0° F." Presumably, these are the properties of the Diesel oil cut of a Fischer-Tropsch "crude" produced by a fluid catalyst process utilizing "cheap, rugged, iron catalysts." No further details are available at present.

TABLE XII

Comparison of Fischer-Tropsch, Tar Oil, Fischer-Tropsch-Tar-Oil, and Petroleum Diesel Fuels [2]

	Fischer-Tropsch	*Tar Oil*	——*Mixture*—— *Untreated*	*Treated*	*Petroleum Gas Oil*
Specific Gravity	0.760	1.060	0.862	0.865	0.857
Colour	Water Clear	Black	Brown Opaque	Yellow Translucid	Yellow
Flash Point (P-M), °F.	120	235	158	158	194
Pour Point, °F.	−4	32	−4	−4	−22
Boiling Index, °F.	420	500	500	500	525
Conradson Carbon, %	0.03	0.26	——	0.004	0.05
Sulphur, %	0.00	0.80	0.40	0.10	0.5
Low Heat Value, B.Th.U./lb.	18,800	17,850	——	18,600	18,600
Hard Asphalt, %	0.00	2.5	0.46	0.03	0.06
Insoluble in Benzole, %	0.00	4.8	0.87	0.05	0.11
Cetane Number	96	20	60	60	50

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Chapter 14

PARAFFIN WAXES

THE Fischer-Tropsch product remaining after removal of the Diesel oil and lighter fractions consists of waxes of various melting points and molecular weights. A hard wax is also recovered from the catalyst by extraction with gasoline fractions.[5] As previously stated, the wax yield and the type of wax obtained is dependent upon the reaction conditions (particularly the pressure) and the catalyst employed in the synthesis. Higher pressures favour wax production, and the use of ruthenium catalysts results in large yields of waxes which possess exceptionally high average molecular weights.

Synthetic waxes consist of a mixture of normal- and iso-paraffins; i.e., they are aliphatic in nature, while petroleum-derived waxes and those obtained from coal tars contain varying (usually small) quantities of cyclic compounds.[3]

The quantities of wax produced in various types of Fischer-Tropsch operation with conventional cobalt catalysts may be seen by reference to Tables IV, V, and VI. The melting points of these waxes range from 120-240° F., and they have molecular weights as high as 2000.[6, 10] Koch and Ibing [6] published in 1935 a quite detailed study on the composition of Fischer-Tropsch waxes from the cobalt-catalyzed synthesis. When ruthenium catalysts are used, as much as 66 per cent of the total product may consist of solid paraffins. The reaction at 380° F. and 1500 pounds per square inch yields about 6.2 pounds of wax and 3.1 pounds of liquid per 1000 cubic feet of synthesis gas.[8] Pichler and Buffleb[9] used solvent extraction to separate the solid product from the ruthenium synthesis (at 14,700 pounds per square inch). The physical properties of the fractions which they obtained are shown in Table XIII.

In their commercial plants, the Germans separated the Fischer-Tropsch waxes into soft paraffin, slab paraffin, and hard paraffin by fractional distillation, pressing, and sweating.[5] The properties and uses of the waxes have been described by Gale [12] and Hall.[13] The crude paraffin was first topped at about 605° F. to remove Diesel oil components. The residue was then subjected to vacuum distillation and cut at about 840° F. The bottoms consisted of hard paraffin with a melting point of approximately 195° F. The distillate was allowed to cool, and the slab paraffin components (melting at 124-128° F.)

were removed by pressing and sweating. The remainder of the distillate was soft paraffin with a melting point of 85-95° F.

Some experiments had been conducted on solvent extraction of the wax product in order to separate the three types just mentioned. Acetone and gasoline were considered promising solvents, but the work was not very far along when the war ended, and no definite process had been developed.[5]

TABLE XIII

Solvent Extraction of Wax from Ruthenium Synthesis at 14,700 Pounds per Square Inch[9]

Extraction Conditions			
Solvent	*Temperature,* ° F.	% *Soluble*	*M.P.,* ° F.
n-Pentane	90	30-33	123-135
n-Hexane	155	14-17	200-204
Synthine cut	194	14-16	250-252
n-Heptane	208	20-25	264-266
Synthine cut	250	12-15	270-273

	Physical Properties				
	Density		*M.Wt.*	*Viscosity, Centistokes*	
Solvent	20° C.	150° C.	(*Av.*)	150° C.	180° C.
n-Pentane	——	——	——	——	——
n-Hexane	——	0.765	760	6	4
Synthine cut	0.966	0.778	1,750	29	17
n-Heptane	0.978	0.783	6,750	870	410
Synthine cut	0.980	0.786	23,000	35,600	15,800

The Germans converted most of the softer Fischer-Tropsch waxes to fatty acids which then were used in the production of soaps and edible fats.[1, 4] A part of these waxes was also used for the preparation of lubricating oils.[7] The hard wax was sold for use in ceresin. It has been stated that the harder Fischer-Tropsch waxes have excellent electrical properties.[11] However, Martin has said[2] that there was only a very small market in Germany for Fischer-Tropsch hard wax and that it will not be a very important product until new uses for it are discovered. It has even been considered economic to crack Fischer-Tropsch wax to produce gasoline.[11] The chemical processing of Fischer-Tropsch waxes to yield soaps, fats, lubricating oils, etc., are considered in the next few chapters.

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Chapter 15

LUBRICANTS

AS MENTIONED, no lubricants, as such, are directly produced by the hydrogenation of carbon monoxide, since the straight-chain paraffins which are the predominant products of the usual synthesis do not, *per se*, possess lubricating properties. However, some modification of the process, perhaps through addition of another reactant, may make possible a direct synthesis. One British patent[26] claims the production of paraffin wax and lubricating oil by the catalytic reaction of carbon monoxide with a large excess of hydrogen at 482° F. (below 697° F.) under 750 (above 300) pounds per square inch pressure in a hydrocarbon medium (such as anthracene oil) that remains liquid under the reaction conditions and in which a catalyst (such as zinc oxide, magnesium oxide, and iron) is suspended.

Disregarding this possible exception, lubricants have, in general, been produced from Fischer-Tropsch products by one or more of the following types of synthesis: (1) polymerization of the lower olefins, olefins in the middle oil fractions, olefins produced by the cracking of Fischer-Tropsch wax, or olefins produced by the halogenation of paraffins and subsequent dehalogenation; (2) alkylation of aromatics with long-chain Fischer-Tropsch olefins; (3) chlorination of Fischer-Tropsch wax or heavy oils, followed by direct condensation or the alkylation of aromatics with the long-chain chlorides; and (4) treatment of heavy fractions with a silent electric discharge, etc. In some cases, synthesis is followed by saturation hydrogenation, in order to increase stability.

The literature on lubricant synthesis in general and synthesis from Fischer-Tropsch products in particular is already voluminous; a literature search[25] reported in 1945 by one of the authors of this book included nearly 600 references, most of them related in some manner to synthesis of lubricants from Fischer-Tropsch products. Since that time, much valuable information has been published as the result of Allied investigations of German developments.[31]

Martin has testified[4, 30] that Fischer-Tropsch lubricating oils were greatly improved in Germany during the war. The best stock for lubricating oil was reportedly obtained by cracking primary products boiling between 427° and 607° F. or wax with a melting point below 86° F. Such stock had to be filtered prior to cracking in order to

remove traces of cobalt left from the Fischer-Tropsch catalyst, since even small quantities introduced undesirable side reactions. A Dubbs unit was used for cracking at temperatures below 930° F. in the presence of steam. Lubricating oil yields of 55 per cent were obtained from the cracked product; most of the oil had a viscosity of about 325 Saybolt universal seconds (SUS) at 122° F. and a viscosity pole height of 1.7. Attempts were made to produce higher viscosity oils by operating at lower temperatures.

Atwell and Schroeder[5] have described in detail Rheinpreussen's synthetic lubricating oil plant at Homberg. Fischer-Tropsch middle oil of approximately 482-662° F. boiling range was chlorinated at 176-212° F. until the chlorine content reached 20-25 per cent by weight, then reacted with naphthalene at 158-212° F. in a volume ratio of five to two, in the presence of 8 volumes of a Fischer-Tropsch naphtha fraction (as diluent) and a small amount of either metallic aluminum or aluminum chloride catalyst. After sludge separation, neutralization, filtration, and naphtha stripping, the product was vacuum distilled to yield spindle oil and turbine oil as overhead and cylinder stock as bottoms.

The fractions were used straight or in blends as motor oils. While Dr Albert Meusel, the source of the information, claimed that all products had high viscosity indexes and were resistant to oxidation, Petroleum Board tests on captured stocks (Table XIV) did not confirm these statements. Dr Meusel stated that the Conradson carbon and neutralization number of a motor oil blend were increased only slightly by air blowing, but Petroleum Board tests on the summer motor oil shown in Table XIV showed an increase in

TABLE XIV

Petroleum Board Tests on Captured Lubricants[5]

	Spindle Oil	*Turbine Oil*	*Cylinder Oil*	*—Motor Oils*— Winter*	*Summer*
Specific Gravity	0.901	0.928	0.965	0.939	0.938
Viscosity at 100° F., SUS	81.5	203.4	895.8	754.9	864.4
Viscosity at 210° F., SUS	37.0	44.2	244.1	64.0	72.6
Viscosity Index	54.6	50.0	61.0	41.1	67.0
Neutralization Value	<0.05	<0.05	<0.05	<0.05	<0.05
Pour Point	+25° F.	−15° F.	+25° F.	−10° F.	−20° F.
Flash Point (closed)	340° F.	395° F.	525° F.	395° F.	440° F.
Coke No. (Ramsbottom)	0.17	0.24	0.11	0.62	0.72

* The winter grade was supposed to have a viscosity of about 270-300 SUS at 122° F. and to be a blend of 45% cylinder oil, 47% turbine oil, and 8% spindle oil; the summer grade, a viscosity of 400 SUS at 122° F. and a composition of 49% cylinder oil and 51% turbine oil.

Ramsbottom coke of 1.73 (from 0.72) upon use of the British Air Ministry oxidation test, while the viscosity (at 100° F.) was 2.26 times as great as that prior to oxidation.

A 25-ton-per-day plant near Marseilles, France, has been producing lubricants by the following series of steps: (1) the chlorination of highly-paraffinic gas oil (end point, 680° F.) at 194-212° F.; (2) mixing of benzene and dichlorethane at 158° F., in the presence of aluminum chloride; (3) reaction of the chlorinated gas oil and benzene-dichlorethane at 158° F. in the presence of aluminum chloride; and (4) termination of the reaction at 230° F. "To make a ton of finished lubes, 600 kilograms of gas oil, 600 kilograms of benzene, and 160 kilograms of dichlorethane are required"; total reaction time is 6 hours; and "the total quantity of aluminum chloride is 10 per cent by weight. ... The present volumetric breakdown of the products is: recycle gas oil, 20 per cent; transformer oil, 30 per cent; turbine oil, 30 per cent; and steam cylinder oil, 20 per cent."

The claimed viscosity index of 100 for the lubricating oils is attributed to the chemical constitution of the lubricant, which is a polybenzene with a long, saturated chain. The oil "is roughly half aromatic and half paraffinic, giving it both a high viscosity index and a low pour point."[1]

The same report describes a pilot plant at Harnes, France, which uses a process developed in Germany to prepare lubricants by the polymerization of a Fischer-Tropsch gasoline containing 50 per cent olefins, produced by lowering the normal hydrogen-carbon monoxide ratio of the synthesis reaction from 2-1 to 1-1 and by raising the reaction temperature. The lubricant synthesis takes five hours in the presence of 3 per cent aluminum chloride; the resulting products are a gas oil, a light lubricant "suitable for cold service, and a heavy lube for ordinary lubrication. ... The quality of these lubricating oils is not exceptionally good. The 'oiliness' is poor, and the oils apparently oxidize readily."[1] In this connection, it is interesting to note[4] that in some German plants "the oxidation test has been improved by inhibitors, the best one being phenthiazine." According to a recent British article[7] and earlier German articles,[16, 17] polymerization of olefinic Fischer-Tropsch fractions produced from water gas yields oils of higher viscosity index and greater oxidation stability than the corresponding operation with olefins produced from synthesis gas.[27] This is not believed to be simply the result of a higher concentration of olefins in such fractions, but rather of a difference in the types of olefins present in the fractions; namely, the proportion of α-olefins to β-olefins. The former predominate in fractions from water-gas conversion and are believed to be largely

responsible for the better viscosity-temperature properties of the synthetic lubricants obtained therefrom.[17]

British experiments[7] indicate that, if moderately viscous oils of good viscosity index are desired, they may be best obtained by the aluminum chloride polymerization of olefins from the 285-395° F. Fischer-Tropsch fraction obtained from water gas. This fraction, as it happens, is somewhat too low in volatility and octane number for large-scale inclusion in gasoline and somewhat too volatile for use as Diesel oil. The higher fractions (b.p. above 340° F.), obtained by cracking the Diesel oil, yield viscous oils of greater oxidation stability than the lower fractions (b.p. below 340° F.),[28] but it has been shown that the oxidation stability of olefin-polymer oils is independent of chain length.[29] Incidentally, Storch [22] reports that the synthesis of lubricants by the direct catalytic polymerization of the olefins produced in the Fischer-Tropsch synthesis has received more attention than synthesis by any other method.

The major portion of the synthetic aviation lubricating oil blending stock produced in Germany during the war was made by the polymerization of ethylene in the presence of aluminum chloride ("Standard Oil process and patent"). The ethylene must be of high purity; it is polymerized at about 250° F. in the presence of aluminum chloride (containing about 4 per cent ferric chloride) under 60-100 atmospheres pressure. A commercial yield of 80 per cent is claimed, and it is said that the viscosity index may be as high as 120, depending primarily upon the temperature and the time of reaction.[2, 11] The ethylene was generally obtained by the cracking of ethane or the hydrogenation of acetylene; it can, of course, be obtained from refinery (cracked) gases or by the deliberate cracking of propane, gas oil, etc. Holroyd[12] reports that "the whole secret of the (lubricant) process is the final purification of the ethylene" and that the process "is definitely superior to any corresponding process developed by the Allies."

According to the Deutsche Fettsaure Werke, the best German synthetic lubricating oil was made by blending 90-95 parts by weight of ethylene polymer with 5-10 parts of an ester of pentaerythritol and C_5-C_{10} fatty acids. The purpose of the ester component was to raise the viscosity index and lower the pour point.[14]

It is interesting to note, incidentally, that one German process called for the reaction, in the presence of aluminum chloride, of an olefin polymer and a de-asphalted, de-waxed, *but not solvent-refined* petroleum lubricant distillate.[13] Whereas 1.5 volumes of de-asphalted and de-waxed distillate were needed to produce 1 volume of oil meeting aircraft specifications by solvent extraction,

0.5 part being discarded as low-grade extract, the mixed polymerization with aluminum chloride produced approximately 3.0 volumes of lubricating oil from the same 1.5 volumes of distillate and 1.5 volumes of ethylene polymer. The oil produced was as good or better than that which was obtained by mixture of solvent-refined petroleum oil and ethylene polymer, so that the net effect of the use of this process was the conversion of 0.5 volume of low-grade extract to satisfactory lubricating oil or, in other words, an increase of 20 per cent in the yield of aircraft oil (from 2.5 volumes to 3.0 volumes).[21] It would appear that the polymer reacts not only with the unsaturates in the mineral oil distillate but also with the aromatic compounds in the potential extract phase. The resulting lubricant is said to be of high quality.

In this process, ethylene is first polymerized with aluminum chloride and the resulting mixture (containing about 5 per cent aluminum chloride) is agitated in an autoclave with an equal weight of petroleum distillate for 3-4 hours at 210-250° F. Table XV shows the yield and properties of such an oil.

TABLE XV

Yield and Properties of Oil from Aluminum Chloride-Catalyzed Mixed Polymerization [21]

	Petroleum Distillate	*Ethylene Polymer*	*Mixed Polymer*
Input, Parts by Weight	52.5	47.5*	—
Output, Parts by Weight	—	—	93.5**
Density at 68° F.	0.915	0.855	0.870
SUS at 100° F.	540	2950	1200
SUS at 210° F.	58	205	108
Viscosity Index	54	109	108
Flash Point, °F.	428	428	428
Pour Point, °F.	±0	−22	−22
Conradson Carbon, Weight %	1.09	0.08 (est.)	0.15

* To produce these 47.5 parts of ethylene polymer, 63.3 parts of ethylene are required.

** In addition, 5.1 parts of low-molecular-weight material are produced.

Storch, in his excellent recent survey on the Fischer-Tropsch process,[22] quotes various German experimenters to the effect that the large increase in viscosity noted in the oxidation of lubricants produced by Fischer-Tropsch olefin polymerization is "associated with the formation of acidic and saponifiable substances, although the amounts of asphalt or coke formed are extremely small. ... Thorough hydrogenation of the oil increased the chemical stability."

Koch[15] reports that such synthetic lubricants contain one or two double bonds and about one naphthenic ring per molecule. Kreulen,[18] however, upon hydrogenating two polymer lubricants, determined that some 50 per cent of the carbon atoms occur in the branched paraffin chains and that these oils contain either 1.2-1.8 or 2.3-4.0 rings per molecule, depending upon the type of test employed.

The hydrogenation of lubricants derived from Fischer-Tropsch oils is said to yield lubricants of higher viscosities, although little effect upon viscosity index is reported. Differences in certain of the finished oils are said to depend upon the variation in the olefin concentration and the constitution of the olefin isomers initially present.

"Excellent ester lubricating oils ... having very high mean molecular weights" were reportedly made by the Germans through reaction of OXO-derived carboxylic acids and alcohols. Long-chain olefins were produced by aluminum chloride polymerization, reacted with carbon monoxide and hydrogen over conventional Fischer-Tropsch catalyst (the OXO process) to produce aldehydes and alcohols, and the aldehydes were converted to the corresponding carboxylic acids by atmospheric oxidation. The ester-oils produced therefrom are said to have possessed good viscosity-temperature characteristics and pour points of 84° F. or lower.[14]

Koch[10] is quoted as reporting that the Fischer-Tropsch process yields alpha olefins as the most likely primary products, beta olefins then being formed by isomerization. An increase in the ratio of hydrogen-carbon monoxide increases the concentration of beta olefins; "a higher operating pressure gives more alpha olefins; the use of an iron catalyst (at 10 atmospheres pressure) produces a higher concentration of alpha olefins (than does cobalt at normal pressure)."

According to the previously-quoted testimony of Martin,[26, 30] the production of Fischer-Tropsch waxes is more economic with the usual cobalt catalyst than with very high wax-yielding ruthenium catalysts, although this logic appears based on "the extreme scarcity of ruthenium." Wax, as mentioned, is an important raw material (via cracking or chlorination) for the synthesis of lubricants, and reference to further details may be found elsewhere in this chapter.

No attempt will be made here to detail the general literature references on the synthesis of lubricants from Fischer-Tropsch products, since these were reported in detail in 1945,[25] as mentioned. Among the more important primary references are 8 and 9, while other reviews include references 6, 13, 19, 20, 22, and 24.

It is by no means certain that the more recent German data have answered all of the questions in regard to the quality of lubricants derived from Fischer-Tropsch oils, since a considerable discrepancy

may be noted between certain German claims and Allied tests on captured oils. Nevertheless, it still appears true that satisfactory (even excellent) lubricants can be produced by several different methods from the primary products produced by normal (paraffin- and olefin-producing) Fischer-Tropsch processes.

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Chapter 16

BY-PRODUCTS

AS MENTIONED, the Fischer-Tropsch process yields primary products which are fertile source materials for chemical synthesis. In fact, one German (Lurgi) chemist, Dr H. Oetken, has even gone so far as to state[22] that the Fischer-Tropsch process "is extremely important, particularly from the point of view of production of chemicals rather than light fuels."

In general, the methods of chemical synthesis used in converting Fischer-Tropsch products into other substances are much the same as those which have been studied or used for the preparation of "chemicals" from petroleum.[28] The actual products, however, often differ markedly, for the Germans concentrated upon the synthesis of products which were usually of natural origin and were not available in Germany in sufficient quantities. Economics, in many cases, were disregarded, and some of the products were *ersatz* in both the German and American sense. However, many are of present or potential interest in America and elsewhere.

Fatty Acids

The Germans particularly excelled in the production of fatty acids by the catalytic oxidation of Fischer-Tropsch paraffin wax.[2, 31, 33] Such synthesis has recently been extensively reviewed,[26] and the basic details (applicable, to some extent, to paraffin wax from crude oil) have been known for some time. Incidentally, it is interesting to note[4, 24] that small percentages of fatty acids (perhaps 0.35 per cent by weight of the main liquid hydrocarbon product) are formed during the normal Fischer-Tropsch process, and "it is by no means impossible that direct synthetic production of fatty acids (perhaps by a Synthol-type variation) will yield high-molecular acids in addition to the mixture of formic, acetic, and propionic already obtained as a by-product of present processes."[4]

Storch reports, in his recent survey,[25] that, while the oxidation of paraffins is strongly exothermic, the process can be controlled to yield chiefly monocarboxylic acids. Operating conditions of 284-320° F. are reported, with the use of 16 cubic feet of air per pound of wax in the presence of such catalysts "as manganese and other metal salts of fatty acids." In his recent general survey, Thompson[27] quotes several authorities to the effect that the C_{20}-C_{35} Fischer-Tropsch

fraction (boiling above 662° F.) is most suitable for oxidation, chiefly with manganese salts as catalysts. Both Storch and Thompson mention, in passing, a British patent[30] which describes the oxidation with hydrogen peroxide of Fischer-Tropsch olefins of C_6 and higher, such as a Fischer-Tropsch naphtha containing 50 per cent mono-olefins.

Conradi, upon interrogation,[6] has mentioned laboratory work at Oppau in which oxidation tests were carried out at 302° F. and at 15-20 atmospheres pressure, "using a cobalt catalyst which, however, proved troublesome because it gave inconsistent results." Quirk[22] states that "Castrop-Rauxel soft wax was going to the Deutsche Fettsaure for oxidation to fatty acids."

One report[9] describes in detail the operations of the Deutsche Fettsaure plant at Witten in the Ruhr. This plant had a capacity of

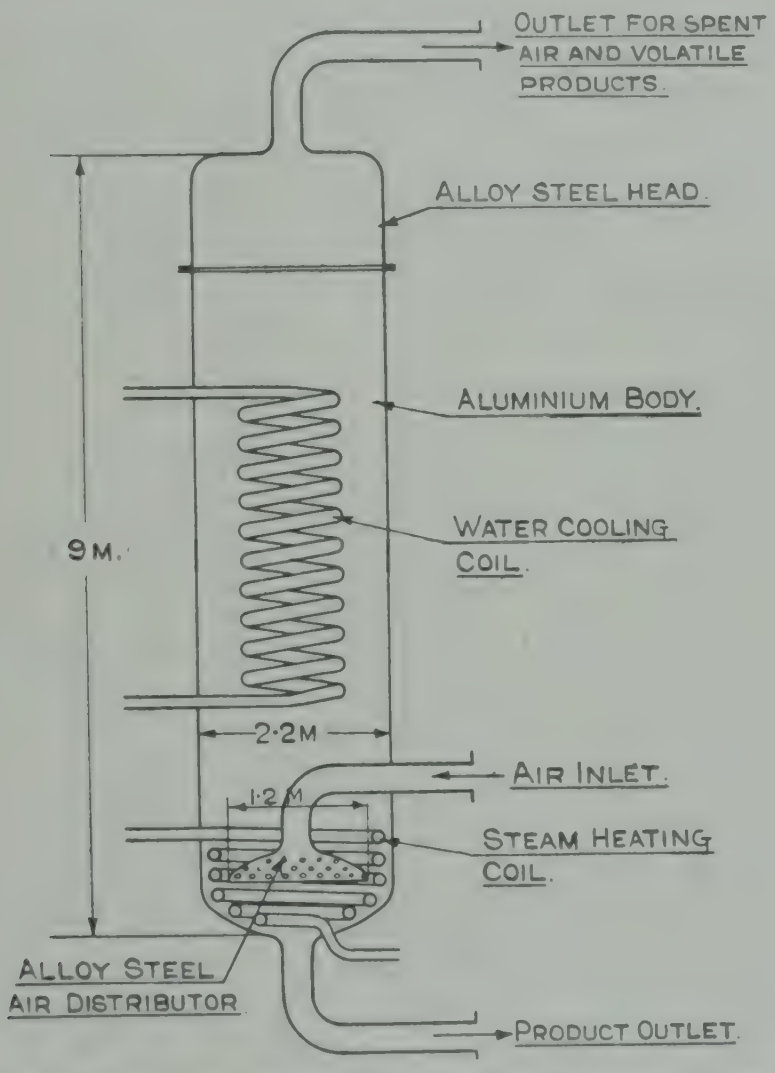

FIG. 15. *German wax oxidation kettle for the production of fatty acids.*

40,000 tons per year of fatty acids and was one of three similar works in Germany, the others being of 20,000 tons annual capacity. A fourth plant, designed to operate under 25 atmospheres pressure, was under construction at Magdeburg; Imhausen "claims that this process is six times more expensive than that used in his plant."

The process used at Witten comprises the charging of 8-20 tons of Fischer-Tropsch paraffin wax and 0.2 per cent of $KMnO_4$ in 15 per cent aqueous solution at 230° F., reacted with 17,655 cubic feet of air per hour per ton of wax for 20-24 hours. The wax charge consists of one part of fresh wax to 1.8 parts of recycle "USM" (unsaponifiable material). Upon completion of the oxidation, a sequence of washing, neutralizing, saponifying, heating, distilling, and acid hydrolysis steps, followed by vacuum distillation, yields the synthetic acid fractions described in Table XVI.

TABLE XVI

Various Synthetic Fatty Acid Fractions[9]

	Light Fraction	*Main Fraction*	*Heavy Fraction*	*Residue*
Temperature, °F.	<248	248-517	517-597	—
Yields, %	15-20	55-60	7-12	7-13
Molecular Weight	C_8-C_{10}	C_{10}-C_{20}	C_{21}-C_{28}	—
Neutralization No.	450-460	245	155-160	80-90
Saponification No.	450-460	255	175-180	110-120
Esterification No.	0-1	10	20	30
Esterification No. for Edible Fats	—	1.5	10	—
Unsaponifiable Matter, %	0	1.5	10.0	—
Unsaponifiable Matter, % for Edible Fats	—	About 1	—	—

The reactor used is shown in Figure 15. Aluminum is the most satisfactory (noncatalytic) material, although alloy steel heads are necessary because "aluminum is corroded by the low molecular weight volatile fatty acids."

All of these plants are said to operate under "the same method as that worked out by the Jasco Co. of America who hold licences from I. G. allowing them to use the patents";[10] these patents, incidentally, were among those whose seizure by the Alien Property Custodian has recently been upheld in a decision by Federal Judge Wyzanski.

According to both these reports,[9, 10] the first fraction, the C_1-C_4 acids, "are recovered from the effluent gases by cooling and adsorption in water. The formic acid (in Germany) is used mainly for the treatment of fodder silos, the acetic and butyric for the esterification

of cellulose, and the propionic (in the form of calcium proprionate) as a preservative in bread."

The C_5-C_{10} acids, obtained as the first product from the vacuum distillation, are further distilled into C_5-C_7, C_7-C_9, and C_9-C_{11} fractions. The first two yield higher alcohols upon hydrogenation, these in turn being reacted with phthalic anhydride to yield alkyd resins; the last fraction is normally used for the separation of minerals by flotation. The C_7-C_9 fraction also finds use in fire extinguishers of the foamite type.

The C_{10}-C_{18} fraction, also separated by vacuum distillation (at 3 millimetres pressure), is used directly in the manufacture of soaps and edible fats (as described later), although, in the production of the latter, the C_9-C_{16} fraction is usually employed, following removal of dicarboxylic acids by treatment with dilute sodium hydroxide.

The next higher fraction, the C_{18}-C_{24} acids, are also separated by vacuum distillation at 3 millimetres pressure. These acids have been used in greases, as softening agents for leather (in combination with triethanolamine), and (as zinc, magnesium, and calcium soaps) as lubricants for plastic moulding. Moulding agents for foundry cores, "artificial petrolatum," and softeners for plastics (certain alcohols and glycols, produced by hydrogenation) have all been produced from the pitch residue.

Edible Fats

Quantities of edible fats have been produced in Germany by the saponification with glycerine of selected Fischer-Tropsch fatty acids; at least 90 per cent of fats so produced can be assimilated by the body, although the suitability of the fats for human consumption has been disputed by German physiologists.[31, 35] Incidentally, it is interesting to note that these fats—and other products produced from synthetic fatty acids based upon Fischer-Tropsch paraffin wax—contain acids of both odd and even numbers of carbon atoms, unlike those produced naturally, which possess only even numbers of carbon atoms. About 150 tons of these edible fats were produced monthly at Witten; "appearance and taste are very similar to oleomargarine."[9]

This report[9] contains a flow sheet showing saponification of the C_8-C_{20} acids (3-4 per cent in excess) with glycerine in the presence of 0.2 per cent metallic tin at 392° F. and 2 millimetres pressure. The triglyceride formed is washed with acid to remove the catalyst, neutralized, treated with active charcoal and bleaching earth, filter pressed, steamed at 392° F. under 2 millimetres pressure, emulsified

with 20 per cent of water, chilled, milled, and sold for vitamin addition.

Soaps and Synthetic Detergents

Soaps were produced in very large quantities from Fischer-Tropsch fatty acids, but it is admitted[9] that the German producers, even with only 30 per cent Fischer-Tropsch soap in the final product, "had not succeeded in removing the characteristic Fischer-Tropsch odour when washing hands. This odour is apparently due to a slight hydrolysis of the soap, and the odour is reminiscent of butyric acid." The causes of the smell are not fully known, and may be connected with the presence of branched-chain fatty acids.[35] As mentioned by Hall and Haensel,[10] the C_{10}-C_{18} fatty acids are used in soap manufacture; the latter process apparently does not differ from the standard methods of making soaps from natural fatty acids.

Although the Germans intended to use the Fischer-Tropsch process to obtain primary alcohols suitable for the preparation of sulphate ester detergents, the only detergents of Fischer-Tropsch origin which were produced on an industrial scale were the hydrocarbon sulphonates made by the sulfochlorination of paraffins and known as "Mersolates".[22, 31] Keunecke[10] is recorded as being "aware of the existence of a soap powder substitute which contained no fatty acids ... produced to the extent of 60,000 tons per annum by the Leunawerke at Merseburg under the trade name of MERSOL."

The process is described in several reports.[12, 31, 33] Fischer-Tropsch gas oil of 446-624° F. boiling range and an average, straight-chain length of 15 carbon atoms was first catalytically hydrogenated at 571-661° F. and under 200 atmospheres pressure, in the presence of a nickel tungstate catalyst (in order to remove oxygen compounds and unsaturates), to yield a mixture of paraffin hydrocarbons known as "Mepasin"; this product was then treated with sulphur dioxide and chlorine at 86-104° F. while undergoing irradiation with "ultra-violet" light. The primary product, known as "Mersol", had the type formula $C_nH_{2n+1}SO_2Cl$, while compounds of the formula C_nH_{2n}-$(SO_2Cl)_2$ were produced as secondary products.

The reactors were vertical steel towers, 20 feet high by 8 feet inside diameter, "the bottom or reacting section of each of these containing 16 glass tubes of 7-inch inside diameter running across the steel cylinder in a horizontal position. In each of these there were placed six 40-60 W daylight lamps (of the type which start on a tungsten filament, then operate as a mercury vapour light). ... The reacting section was 8 feet high." The entire reactor and all pipe lines were lined with an acid resistant resin of the "Haveg" type, and the

upper part of this vessel was filled with rings of the same composition. The Fischer-Tropsch fraction entered at the top, while the chlorine and sulphur dioxide entered at the bottom. Other equipment details have also been given.[12]

"The reaction is carried to only 70 per cent of completion, as too much disulphonyl chloride is formed if it is attempted to react more than this percentage of the oil. The product, for the most part, was shipped to soap makers (who saponified it together with their other soap making materials). ... The product as made contained 30 per cent unreacted oil and about 70 per cent of sulphonyl chlorides. Of the 70 per cent, 50-60 per cent was monosulphonyl, the remainder being a mixture of di- and higher sulphonation products which are useless in the soap which is made from the Mersol."[12]

The Mersol was saponified (at 158° F. with 10 per cent NaOH solution) to the commercial product "Mersolat", which was used mainly as a soap powder in admixture with water-glass or Tylose (a cellulose product). The product was believed to have a peacetime future for wool-washing and as an emulsifier in polyvinyl chloride and Buna rubber manufacture.[34] A cresol ester of Mersol was also used to plasticize polyvinyl chloride.[12]

It has been reported[19] that the detergent produced by saponifying Mersol "was of very inferior quality. A later product called Mersolat H, made by a somewhat modified process, was considerably better....

"Some of the better known Igepons (high-grade detergents) were derived from oleyl chloride, made from synthetic oleic acid by condensation with the sodium salt of hydroxy-ethanesulphonic acid or the sodium salt of methyltaurine."

Detergents of the Igepal variety, made by condensing ethylene oxide with fatty alcohols or alkyl phenols, were "suitable for washing cotton and rayon" when containing 10-14 oxyethane groups and "excellent for emulsifying mineral oils" when having 20-30 oxyethane groups. "The introduction of a sulphonic group changed the Igepal from a non-ionic to an anionic detergent.

"A great deal of work was done on emulsifiers, the Emulphors being perhaps the most important." One of these was the cyclohexylamine salt of Mepasin phenol-sulphonic acid and another the sodium salt of Mepasin sulphamidoacetic acid. These were such excellent cutting oils and drawing compounds that their use was almost entirely restricted to these important war needs. They were quite outstanding for this purpose because they were emulsifiers which had great metal affinity and because they contained a rust-preventing polar group.[19] Other detergents and emulsifiers derived from Fischer-Tropsch products were also prepared by the Germans.

Lubricating Greases

Greases, apparently, were also produced in appreciable quantities from soaps of oxidized paraffins and from either synthetic or mineral oils. As mentioned, the C_{18}-C_{24} fatty acids from the oxidation of Fischer-Tropsch paraffin wax "have found application in greases as sodium, calcium, and lithium soaps. ... The zinc, magnesium, and calcium soaps have also been used as lubricants for plastic moulding. ...

"In connection with the use of the C_{18}-C_{24} acids in grease manufacture, Dr Keunecke was asked if he knew anything of developments in Germany on tropical greases, and he stated that they had found that the addition of 2 per cent of calcium benzoate to a soda base grease made with synthetic fatty acids would render it water-resistant without lowering the melting point, which was of the order of 392° F. The exact proportion of benzoate was varied a little according to the type of fatty acid concerned."[10] Some miscellaneous information on greases is contained in a recent report.[8]

The "OXO" Process

In addition to those alcohols produced as part of the primary products of the German (and perhaps American) "Synthol" processes; to those produced by deliberate synthesis over special catalysts under specific conditions, such as methanol and isobutanol; and to those prepared (as mentioned) in the conventional manner by sulphuric acid hydration of the corresponding olefins, such as amyl and hexyl alcohols, the Germans were preparing at the close of the war to produce 8,000 to 10,000 metric tons of alcohols per year in a Ruhrchemie plant by the "OXO" process.[29, 31, 32]

This process involves the treatment with carbon monoxide and hydrogen of such olefins as a Fischer-Tropsch C_{11}-C_{17} fraction at 275-302° F. and 150-200 atmospheres pressure containing in suspension a cobalt-containing regular Fischer-Tropsch synthesis catalyst, followed by reduction of the resulting aldehydes at 355° F. under 150 atmospheres over either similar catalysts or such cheaper catalysts as those containing nickel.[22, 29]

The raw material to be used in the Ruhrchemie plant at Holten was the fraction 175° to 310° C. of primary or cracked Fischer-Tropsch oil containing 45-50 per cent of olefins. This material was cut into four fractions (C_{11}-C_{12}, C_{13}-C_{14}, C_{15}-C_{16}, and C_{17}), in order to facilitate subsequent separation of the alcohols, which were treated separately.[29, 31, 32, 34]

Magnesium was excluded from the catalyst for the first stage "if at all possible." The sulphur-free water gas contained 39 parts of

carbon monoxide to 45 parts of hydrogen. "The process was intermittent, each cycle taking 20 minutes"; temperatures were controlled by means of steam pressure.[21]

Olefins "having from two to at least 20 carbon atoms"[29] can be converted into aldehydes by the first step of the process; for example:

$$\underset{\text{Propylene}}{C_3H_6} + CO + H_2 \rightarrow \underset{\text{Butyraldehyde}}{CH_3CH_2CH_2CHO}$$

FIG. 16. *Ruhrchemie alcohol plant.* (Courtesy of W. C. Schroeder, U.S. Bureau of Mines.)

It was claimed[21] that adipic acid could be made by oxidation of the hexandial produced from alpha-butylene or butadiene. In addition to the primary use of the alcohols produced from C_{11}-C_{17} Fischer-Tropsch olefins—the production of sulphonic ester detergents—"plasticizers were also made by applying the OXO process to the C_7-C_{10} olefin mixtures and subsequently forming the phthalic acid ester of the alcohols produced."[29]

A process called the "Synol" process has been mentioned in considerable detail in references 15 and 29. This process, similar perhaps to the "Synthol" process, produces alcohols directly from carbon monoxide and hydrogen over a specially-reduced iron catalyst at 364-383° F. under 20-25 atmospheres pressure. The alcohols (60 per cent of the product) are fairly evenly distributed over the whole boiling range of the product. They are straight-chain alcohols, and

the mechanism of their formation cannot therefore involve the OXO reaction which gives branched-chain alcohols.[31]

Returning to the OXO process, the aldehydes produced in the first step can, if desired, be separated and marketed as such, although there is "considerable conversion of aldehydes to alcohol ... in the first stage," which prevents high aldehyde yields, based on the olefins.

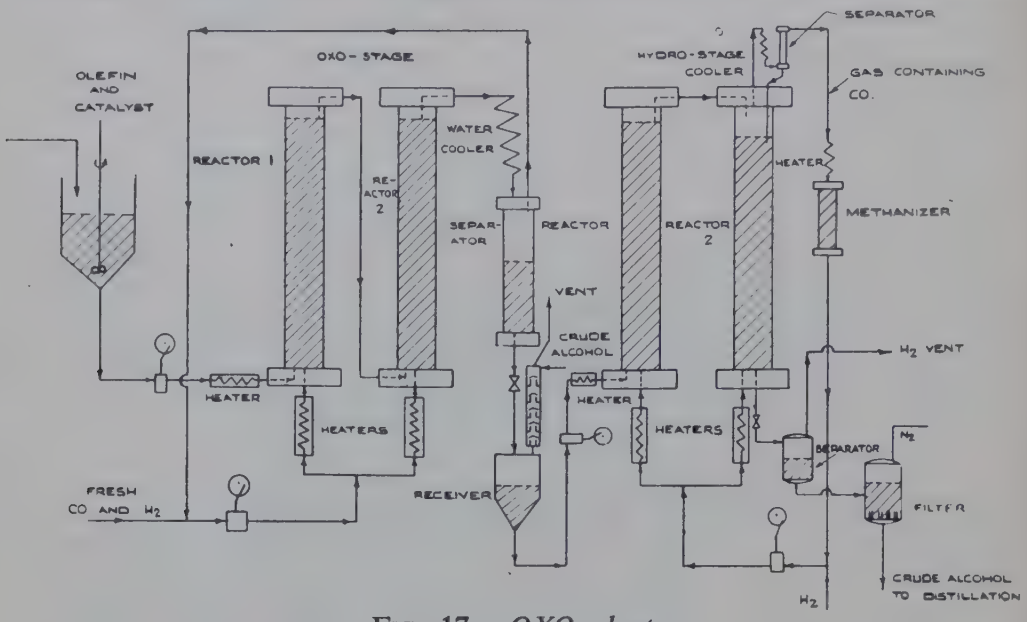

FIG. 17. *OXO plant.*

In fact, the Germans recommend production of the alcohol by the OXO process, then oxidation back to the aldehyde when the latter is desired.[29] Many further details of the OXO process and its products are contained in other reports.[15, 29, 32] As originated by Ruhrchemie A.-G., the OXO process was a batch operation. However, the co-operative efforts of Ruhrchemie and I. G. Farbenindustrie resulted in the development of a continuous process, the operating details of which are contained in references 15 and 32.

Miscellaneous Chemicals

In addition to the chemical products already mentioned, numerous other derivatives can be produced from Fischer-Tropsch primary products or from the basic reactants, carbon monoxide and hydrogen.

According to reference 4, formaldehyde synthesis may become possible if sufficiently high pressures and active catalysts can be achieved; "Professor Fischer himself regards it as not impossible to synthesize even carbohydrates," a hope perhaps "too theoretical to arouse practical interest." Among reactions on Fischer-Tropsch products not previously mentioned in detail in this book, however, are the following selections from a list by Fischer:[23]

"Addition of carbon monoxide and water to olefins to make acids;
"Addition of carbon monoxide and water to alcohols to make acids;
"Production of glycols from olefins;
"Isomerization of paraffins; e.g. hexane to neo-hexane;
"Alkylation, thermal and catalytic;
"Aromatization;
"Conversion of isobutylene to Butyl rubber and high polymers;
"Polyhydric alcohols from olefins and paraffins via chlorination; e.g. glycerol;
"Carboxy-chlorination of paraffins; etc."

Many of these reactions, as mentioned, are identical with those used in the synthesis of chemicals from crude petroleum and its fractions. Others, however, are not in general use.

Isobutanol, for example, was synthesized from hydrogen and carbon monoxide (18-20 per cent of the latter) in yields of 10 per cent (plus 55 per cent yields of methanol and 13.8-15.8 per cent of higher alcohols) under pressures of 300 atmospheres in special converters; "methanol was recycled to the reaction." Conradi states that isobutanol was made at Oppau, Leuna, Heydebreck, and Auschwitz "by a variation of the methanol synthesis ... at a temperature approximately 180° F. higher than that used for methanol synthesis at 200-300 atmospheres pressure, and at a lower space velocity. The standard methanol catalyst is used, but with the addition of alkali."[6]

The isobutanol so produced was dehydrated to yield isobutylene and then converted into isooctane; 40,000 tons per year of the latter were produced by this process at Heydebreck.[16] The higher alcohols produced at this plant were hydrogenated to yield isoparaffin hydrocarbons which were also used in aviation gasoline blends.

It is worthy of note, incidentally, that the "Hydrocol process"[17] will produce, as by-products from 64,000,000 cubic feet of natural gas per day, 150,000 pounds *per day* of "crude alcohols in water solution," consisting chiefly of "acetaldehyde, acetone, and ethyl, propyl, butyl, amyl, and heavier alcohols."

At Leuna, alkylbenzenes were produced using C_7 and C_8 alcohols "from the higher alcohol process."[16] The same report states that "glycerine was made at Heydebreck from propylene made by dehydrogenation of the propyl alcohol from higher alcohol synthesis ... (production of) 2,000 tons per year was achieved."

"Aldehydes were made at the Leuna plant from the alcohols

produced there. Fatty acids were also made at this plant from the highest fractions of the alcohols remaining from isobutanol manufacture by caustic fusion and precipitation with sulphuric acid."[12] A castor oil substitute was prepared by esterifying some of these acids with trimethylolethane; the remainder were used for the production of "Solagen" driers in the form of cobalt and manganese salts.

Some of the isobutylene produced at Oppau was used for the production of polyisobutylene, known in Germany as Oppanol and in the United States as Vistanex, etc. Ethylene was added to the isobutylene, and the latter was then polymerized on a moving steel belt at −150° F. "by allowing the ethylene to evaporate; it was then recompressed and used again. The catalyst, one per cent of boron trifluoride, was added at the beginning of the belt."[6] Conradi stated that Oppanol was being used to raise the viscosity index of lubricants and as cable insulation. "It is already known that the addition of one per cent of butadiene prior to polymerization enables the final product to be vulcanized";[6] this is similar, presumably, to Butyl rubber.

Various other materials can be produced. By-products of Fischer-Tropsch wax oxidation include dicarboxylic acids and various aldehydes, alcohols, and ketones.[18] Sulphonic acids obtained from Fischer-Tropsch hydrocarbons have been used for the preparation of water-soluble cutting oils.[11] Ketones for use in the cosmetics industry or as plasticizers have been produced by the saponification with lime of Fischer-Tropsch fatty acids; the resulting calcium salts are destructively distilled at atmospheric pressure and the crude product redistilled under vacuum. Since most of the ketones produced from a heterogeneous mixture of fatty acids boil between 464-571° F. and have melting points between 14° and 86° F., it has been assumed that these ketones contain 12-17 carbon atoms.[3, 5, 20]

The above ketonization, followed by hydrogenation, is used on the pitch residue of the distillation of Fischer-Tropsch fatty acids to yield long-chain saturated hydrocarbons "which are claimed to be an excellent substitute for petrolatum."[10] The heavy cut from the aluminum chloride polymerization of Fischer-Tropsch olefins, previously described under synthetic lubricants, has been used in France to produce "a substance similar to petrolatum, which is being used by the cosmetic industry" by hydrogenation at 392° F. under 100 atmospheres pressure over standard (cobalt-thoria-magnesia-kieselguhr) Fischer-Tropsch catalysts.[1]

Variations of the Fischer-Tropsch process, described in Part II of this book, are "iso-synthesis" and the synthesis of aromatic hydro-

carbons.[7, 13, 14] These processes make possible the preparation of a wide variety of isoparaffins, aromatics, and naphthenes, and, if economic, will serve "to round out" the Fischer-Tropsch process as a source of chemical materials. Space here does not permit discussion of methanol synthesis from carbon monoxide and hydrogen, but this process is in wide use and is well understood.

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Part IV

ECONOMICS OF THE FISCHER-TROPSCH PROCESS IN THE UNITED STATES

Chapter 17

THE PETROLEUM SITUATION

THE preceding sections of this book have contained sufficient details to prove beyond any reasonable doubt that variations of the Fischer-Tropsch process are capable of producing any or all of the multiplicity of present-day "petroleum" products. German operations, also, have conclusively shown that many of these Fischer-Tropsch variants may be readily applied in full-scale operations.

The prior art of the Fischer-Tropsch process is already very large in size and scope, but, just as for all processes, much more may still be accomplished. Future major advances may be expected in the perfection of new process techniques (fluid catalyst, etc.), the development of new catalysts, the improvement of equipment, and the better refining of the products. More economic methods of synthesis gas production, such as continuous gasification and perhaps even underground gasification of coal, will probably be technically perfected.

Whether or not the Fischer-Tropsch process will be extensively applied in America, now or later, depends on economic factors as much as it does upon technical progress. If American petroleum supplies were inexhaustible and were to continue to be available in sufficient quantities to meet all demands at a low cost, interest in the Fischer-Tropsch process—and in other petroleum substitute processes—would be chiefly academic. Similarly, if world petroleum resources were freely available to all nations on the basis of demands —and were to so continue, without artificial production or tariff barriers—there would be little urgency in the present attention to a process which gives no signs of ever materially bettering low petroleum prices even if it does appear potentially capable of meeting them.

Unfortunately, neither of these situations pertains at present. While future discoveries may temporarily halt the trend, increased exploration costs per barrel of oil discovered in the United States portend increased petroleum prices—unless a flood of inexpensive foreign-produced oil eliminates high-cost producers and restricts price advances, even at the expense of profits. This latter development, not at all unlikely unless legislated against by high tariffs or international cartels, would amply provide for anticipated increases in petroleum demands were the flow of imports to continue, once

begun, but the spectre of possible wars rises in front of all planners who consider this the solution to an eventual shortage.

If future wars are at all like past ones, or are long in duration, any nation externally dependent for its petroleum supplies may very well be defeated *ipso facto*, for no navy can *guarantee* that such shipments will continue—and the source of such supplies may conceivably fall into enemy hands. An effective United Nations may ultimately render such a discussion "war mongering", but the cost of adequate preparedness for war is an inexpensive insurance policy if war can thereby be avoided—and a mere bagatelle of vital importance if war should come.

World petroleum resources are undeniably extensive. Joseph E. Pogue has recently released the estimates shown in Table XVII.[2] As can be seen from these figures, the Western Hemisphere, while not as well equipped with potential reserves as the rest of the world, still possesses sizable quantities of oil. However, as Pogue points out, "any attempt to relate proved (or estimated future) reserves to current production and (thus to) calculate the future life in terms of years' supply is fallacious and misleading."

TABLE XVII

Estimated Proved World Oil Reserves and Future Discoveries [2]
(In Billions* of Barrels)

Country or Region	*Estimated Proved Reserves*	*Estimated Future Discoveries*
United States	21.0	50
Caribbean Area	9.0	65
Rest of Western Hemisphere	0.5	30
Total Western Hemisphere	30.5	145
Soviet Union	6.0	100
Rest of Europe	0.8	8
Middle East	27.0	150
Far East (South-west Pacific)	1.0	58
Rest of Eastern Hemisphere	0.5	29
Total Eastern Hemisphere	35.3	345
Grand Total, World	65.8	490

* U.S. Billion = thousand million.

Foreign production prices are tangled in a skein of royalty payments, high taxes, monetary difficulties, and trade restrictions,

but it appears likely that Middle East oil, for example, could immediately compete with domestic crudes in the coastal regions of the United States. This is supported by the fragmentary data that have been published; Tables XVIII and XIX are perhaps typical examples, whose force is intensified by the price increases in U.S.A. since their publication.

TABLE XVIII

Competitive Cost of Middle East and East Texas Oil, F.O.B. New York [1]

(Middle East Oil via Suez Canal)

Middle East	*Per Barrel*
Production cost	$0.10
Royalty average	0.21
Tanker from the Persian Gulf to New York via Suez Canal. Present-day, modern tanker, foreign officers, and crew	0.61
Loading Cost	0.02
Present tax on imported oil from countries having "friendly nations' contracts"	0.10½
Toll charge through Suez Canal	0.13
Total out-of-pocket cost	$1.17½
Difference in refinery realization against Arabian oil	0.20
Total out-of-pocket competitive cost f.o.b. New York	$1.37½

East Texas	
Market price	$1.25
Gathering charge, published rate	0.05
Pipe line to Gulf, published rate	0.10
Loading at Gulf	0.02
Tanker to New York. Present-day, modern tanker, American crew. Foreign crews cannot operate coastal vessels	0.20
Total f.o.b. New York	$1.62

TABLE XIX

Competitive Value of Middle East and California Oil F.O.B. Los Angeles Refineries [1]

Middle East	
Production cost	$0.10
Royalty average	0.21
Tanker from the Persian Gulf to Los Angeles refineries. Modern tanker foreign officers, and crew	0.61
Loading cost	0.02

Middle East (cont.)

	Per Barrel
Present tax on imported oil from countries having "friendly nations' contracts"	$0.10½
Total out-of-pocket cost	$1.04½
Difference in refinery realization against Arabian oil	0.20
Total competitive cost	$1.24½

Kettleman Hills 38 Gravity

Market price	$1.33
Gathering and pipe-line transportation costs	0.17
Total f.o.b. refinery	$1.50

Venezuelan crude oils, of course, have been used in the United States on a competitive basis for some time, as have other Latin American crudes. Continued peace, then, would apparently see a theoretically ample world supply of oil, for foreign demands will certainly not keep pace with production potentials.

However, it would seem that research on and commercial use of such petroleum synthesis methods as the Fischer-Tropsch process are justified for two main reasons: (1) national security and (2) potential profitability. It is with these two factors that any basic economic analysis must be concerned.

Other Substitute Processes

Before embarking on a detailed analysis, however, it is pertinent to note some of the reasons why the Fischer-Tropsch process receives the greatest attention among all the various methods for the production of petroleum substitutes. Most of these reasons are apparent from Table XX, which is a revision of a table which one of the authors of this book had occasion to prepare a few years ago.[3]

Oil shale and tar sands contain vast supplies of "oil," some of which will undoubtedly prove economic for use, but neither these nor agricultural-derived fuels (not shown) possess the over-all potentialities of Fischer-Tropsch products from coal. Not all the available coal would be so employed, of course—probably not even 50 per cent of the total, for normal coal uses will have to be met—but the implications are clear. Natural gas possesses economic advantages at present levels, as this table shows, but reserves are too small to make it a dominant factor for long.

TABLE XX

Comparison of Leading Petroleum Substitute Methods*[3]

	Raw Materials and Methods					
	Coal		*Natural Gas*			
	Hydrogenation	*Synthine Process*	*Synthine Process*	*Oil Shale*	*Tar Sands*	*Crude Oil*
Total North American Reserves (Billions† of Tons of Source Material)	4,000	4,000	>3	>400	>500	?
Percentage of Total Source Reserves Most Practical for Exploitation	26	50-100	10-25	?	1	?
Potential Gasoline Yield from Most Exploitable Reserves (Billions† of Barrels)	1,500	3,000-6,000	2-4	50	2	10-25
Cost of Gasoline (Cents per Gallon)	15**-24	6**-18	5**-9	8**-15	8-12	6-?
Investment (Dollars per Daily Barrel of Gasoline	6,500**-13,500	2,800**-10,000	2,200-4,770	3,200	1,335-3,300**	1,400-2,800

* Based on published estimates. Coal hydrogenation calculations are based on sub-bituminous coal only, although other types may also be hydrogenated, and coal-Synthine process estimates are based on all types of coal, even though not all types are usable in every synthesis gas process variant. Oil shale reserves include only those which are known to be readily accessible; this is true also for tar sands. Gasoline costs are rough estimates only, with no allowance for by-products or transportation costs, while the value of coal and shale is merely the mining costs. Figures on investment are little more than guess work, since most published detailed calculations are based on obsolete technology; that for crude oil lies somewhere between the two given.

** Indicates the figure reported in the literature which appears to be most credible (at least as to order of magnitude).

† U.S. billion = thousand million.

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Chapter 18

ECONOMICS OF FISCHER-TROPSCH PRODUCTS FROM COAL

COAL, a complex substance composed chiefly of carbon, but also containing varying percentages of hydrogen, oxygen, nitrogen, and sulphur, is present in North America and in other places in huge quantities. Depending upon the proportionate amounts of fixed carbon, volatile matter, etc., coals are ranked as anthracite, bituminous, sub-bituminous, and lignite; they are also classified into various types, depending upon appearance and structure. This brief description hardly serves to describe completely the intricacies of coal classification, but it does serve as a reminder that coal, like petroleum, is not a uniform product from field to field and that its different grades possess varying properties and uses. Anthracite is of high value as a residential fuel and in relatively limited supply, and these factors, coupled with relatively high mining costs, render it improbable that producers of petroleum substitutes would consider this rank of coal for a raw material.

In regard to the effect of rank on use in the Fischer-Tropsch process, it is pertinent to note that those Fischer-Tropsch variations which depend upon water gas made from coke are necessarily restricted to the use of coals with reasonably good coking properties, but more recent processes (specifically, continuous gasification) are applicable to almost all kinds of coal. From a technological standpoint, therefore, the total coal reserve in the United States is theoretically usable for the Fischer-Tropsch process, but naturally, the cheapest grades will be used first unless some offsetting process advantage is found for the more expensive ranks.

It is more than interesting to note that in the U.S. the most important deposits of low-grade coals are found in North Dakota, Montana, Wyoming, and Colorado. Texas deposits are by no means insignificant, however, so that it is far from certain that this state may be ruled out as a major producer of oil from coal by the Fischer-Tropsch process. Many states have large deposits of bituminous coal, so that some of these will certainly bulk large as synthetic oil producers; at the present time, at least, bituminous coal is still *the* coal for the Fischer-Tropsch process.

Incidentally, it has been estimated by Keith[3] that the proved fuel reserves of the United States, if converted to crude oil by the Fischer-

Tropsch process, are equivalent to some 6326 thousand million barrels, a truly staggering figure. Some idea of the importance of coal as the raw material for long-continued use of the process may be obtained from a breakdown of this mythical but qualitatively interesting total: crude oil reserve, 21 thousand million barrels; natural gas converted to Fischer-Tropsch oil, 25 thousand million barrels; coal converted to Fischer-Tropsch oil, 6280 thousand million barrels.

Yields from Coal

Yields of products vary with the catalysts and reaction conditions, as noted in Part II, but some generalities are of interest here. In testimony given in 1943,[2] A. C. Fieldner and Bruce K. Brown both stated that approximately 0.70 ton of bituminous coal is required to yield the coke needed for the (conventional) production of one barrel of Fischer-Tropsch gasoline and to yield the power, process steam, etc., required for the process; this figure agreed with estimates given by Robert P. Russell and Fred Denig. Thus the yield of gasoline per ton of bituminous coal, in the older form of Fischer-Tropsch synthesis, is approximately 1.43 barrels.

For the continuous gasification of bituminous coal, it has been estimated that a yield of 2.3 barrels of gasoline per ton of coal is obtainable; for sub-bituminous coal, the yield is 1.7 barrels of gasoline. The yield from lignite would be still lower, but so might the cost (eventually).

As regards Fischer-Tropsch primary products, A. C. Fieldner[2] has stated that 4 to 4½ tons of coke (the equivalent of 5-6 tons of bituminous coal) are required to yield one ton of primary products. Assuming that the specific gravity of the average crude is about 0.8, it would seem that about 1.2-1.5 barrels of primary products are obtained per ton of bituminous coal used in this process for all purposes (raw materials, fuel, etc.). When continuous gasification is used, a much higher yield is obtainable—perhaps as much as 2.6 barrels. Yields for sub-bituminous coal and lignite would be somewhat lower.

Manpower Requirements

Assuming that coal will eventually be used as the raw material for the Fischer-Tropsch process, it is pertinent to inquire into the manpower requirements necessary for the production of the vast supplies which may be needed. The existing U.S. mines could undoubtedly supply part of the demand, for their capacity has never been reached, but many new mines and a new mining industry would certainly be

needed—unless underground gasification proves a large-scale success. At present, furthermore, there are no substantial mining facilities for the lower ranks of coal (sub-bituminous and lignite) which may be most economically attractive.

In 1941, the average production of bituminous coal per man-day in the United States was 5.2 tons,[8] although strip mining in certain localities yielded much higher quantities (14.23 tons per man-day in 1938, with some localities reporting as much as 68.54 tons per man-day). Using this national average and the calculation that the Fischer-Tropsch process requires 43,500-70,000 tons of bituminous coal for a daily production of 100,000 barrels of gasoline, this gasoline production would require a mining manpower of 8,000-14,000 men. In terms of 100,000 barrels per day of primary products, instead of gasoline, as many as 10,000-15,000 men might be required, as a rough estimate.

For sub-bituminous coal used in the continuous gasification processes, approximately 11,300 men would be required to mine the coal needed for a daily gasoline production of 100,000 barrels. Average production of lignite in 1941 was 9.54 tons per man-day,[1] but Fischer-Tropsch yields from lignite are not at hand; it may be assumed, however, that manpower requirements for mining would be of the same order of magnitude as for the other ranks of coal.

No good data are at hand as to the probable manpower requirements for the actual operation of Fischer-Tropsch plants. One estimate, extrapolated from data for a small-scale (1000 barrels per day) plant, would seem to indicate an operational manpower requirement of 11,500 men for the daily production of 100,000 barrels of Fischer-Tropsch primary products, or 16,400 men per 100,000 daily barrels of gasoline, but it seems possible that these figures are too high to be very reliable.

It is pertinent to note that the drilling for and production of some 1,250,000,000 barrels of petroleum in 1939 (which yielded about 550,000,000 barrels of gasoline upon refining) required some 170,000 workers, and that the refining operations required 100,585 workers. Disregarding transportation employees for purposes of fair comparison, it may be seen that the production of 100,000 barrels per day of crude oil required about 5,000 men in 1939 and that the total manpower required per 100,000 barrels per day of gasoline was approximately 18,000 men.

This last figure is high, of course, since it disregards the fact that an equal volume of products other than gasoline was produced, but it indicates that the production of Fischer-Tropsch gasoline from coal (including coal mining) will have manpower requirements

reasonably equivalent to those for the preparation of gasoline from petroleum (including production.)

The sociological desirability of such production is quite another matter, however. Coal mining, even mechanized, is an industry which seems almost outside the present social pattern (or at least the desirable social pattern). It is possible, of course, that atomic (nuclear) energy may eventually eliminate many of the fuel uses of coal, releasing present mining capacity for "chemical" (process) usage, but this factor is indeterminate in the present state of the art.

The effect of possible use of underground gasification is also incalculable at present. This method was discussed in some detail in Chapter 3, and its chief economic advantage is undoubtedly the reduction (or possible elimination) of underground labour, but the Russian figures, while showing a per-man output (thermal equivalent) of 100-120 tons per month, compared with 30 tons per month by regular mining,[4, 7] are hardly conclusive when it is remembered that the United States average production of bituminous coal was 5.2 tons per man-day in 1941, far above the Russian average. Nevertheless, this method offers economic and sociological attractions and is definitely worthy of additional attention.

Costs from Coal

The cost of producing gasoline (and other products) from coal in the U.S.A. has not yet been clearly determined; as Table XX has shown, estimates vary over a wide range. The higher figures are based on obsolete German technology, however, and P. C. Keith[5] has recently stated that, for a combination of the direct coal gasification and the Hydrocol synthesis process, "six-cent gasoline from $2-per-ton coal is not more than two or three years off."

Robert P. Russell[2] stated in 1943 that a Fischer Tropsch plant of the European coking type, using bituminous coal, yields gasoline at a cost of 19.2 cents per gallon, including 4.5 cents per gallon for 10 per cent depreciation. Fred Denig testified at the same time that the cost of Fischer-Tropsch gasoline from coke (from bituminous coal) would be 24.4 cents per gallon and that the cost would be 18.2 cents per gallon from coke from sub-bituminous coal. While these estimates are based on detailed calculations, their dependence on obsolete European data renders them of little future significance, and it is entirely possible that near-future costs may be as low as 6-8 cents, as the following estimate indicates.

According to E. V. Murphree of Standard Oil Development Company,[6] "a plant to produce about 9,000 barrels per day of gasoline along with some 1,800 barrels per day of gas oil from coal,

using the fluidized (catalyst) technique, is estimated to cost roughly $42,000,000. In addition to the gas oil and gasoline produced, this plant would produce slightly under 40,000,000 cubic feet of around 1000 B.Th.U. gas per day. If this gas is credited at 25 cents per 1000 cubic feet and suitable credit made for the gas oil produced as well as certain chemicals, then the cost of gasoline from this plant based on coal at $2.50 per ton comes out to roughly 7.25 cents per gallon. This is not a great deal more than the cost of production of similar grade gasoline from crude oil at present crude prices. The investment, however, is much higher for the gasoline from coal plant than would be involved in making the equivalent quality of gasoline from oil, and the above cost includes no return on the added investment." Murphree's estimate makes no allowance for returns from the sale of alcohols, acids, ketones, and other organic chemicals produced in the synthesis, but he has pointed out that, "in areas where these chemicals can be disposed of, their production represents an appreciable credit to either the natural gas or coal operation."

Investment Required

The investment required for conventional types of coal mining in the United States has, in the past, ranged from $1-$10 per ton-year, the low figures being for strip mining and the high ones for shaft and difficult strip mining. Taking a yield of two barrels of Fischer-Tropsch gasoline per ton of coal as a rough estimate for modern plants, and $5 per ton-year as a rule-of-thumb investment figure for coal mining, the production of 100,000 barrels of gasoline per day would require an investment in coal mining facilities of about $150,000,000 for a 300-day working year. Much less would be required for strip mining, of course.

According to Robert P. Russell,[2] the investment required for plants to produce 100,000 barrels of Fischer-Tropsch gasoline daily from coal (according to the obsolete European design) would be approximately $760,000,000. Fred Denig[2] has presented figures which yield an estimate of $618,000,000 for pre-war economic conditions, while Bruce K. Brown has given figures which would yield an estimate of $1,000,000,000-$1,667,000,000. According to the previously quoted recent estimate of E. V. Murphree,[6] the present figure might be about $467,000,000.

It has been roughly estimated that the investment figure for synthesis plants may *ultimately* be as low as $100,000,000-$200,000,000 per 100,000 barrels of gasoline daily for plants of future design. It may be seen, therefore, that total investment requirements (including those for coal mines) may eventually be as

low as $2,500-$3,500 per daily barrel of gasoline—possibly of the order of magnitude of those required for the production of gasoline from petroleum.

Steel Requirements

Steel supplies in the United States (except in boom times like the present) are not as critical in peace as they are in war, but it is important to note that considerable quantities would be required for the erection of a large-scale Fischer-Tropsch industry—too great an amount, certainly, for speedy construction in time of emergency. Estimates[2] vary from 8.9-14.3 tons of steel per daily barrel. Thus, plants to produce 100,000 barrels of synthetic gasoline per day would require from 890,000-1,400,000 tons of steel.

These estimates include cracking plants and accessories, which, however, constitute only about 3 per cent of requirements.

For modern plants using continuous gasification and thus avoiding coke production and use, it has been estimated, as a *guess*,* that these earlier figures may be several times too high. If this is correct, steel requirements might eventually be of the same order of magnitude as those for gasoline production from petroleum.

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Chapter 19

ECONOMICS OF FISCHER-TROPSCH PRODUCTS FROM NATURAL GAS

IMMEDIATE commercial application of the Fischer-Tropsch process in the United States is dependent upon the use (and continued availability) of low-cost natural gas. However, gas prices have witnessed an upward trend in recent years, and there has been continued agitation, lately, to restrict the use of this "exhaustible" natural resource to "high-utility" uses based upon its physical state.

There seems to be a general agreement that ultimate reserves of natural gas may be estimated at more than 200 million million cubic feet. E. DeGolyer, in recent testimony before the Federal Power Commission, presented the data shown in Table XXI and has commented further[3] that, "in a broad consideration of this important natural resource, it should be noted that if these reserves are calculated on a pressure of one atmosphere, include the 6,000 smaller fields not included in this estimate, and allow for the extension of present fields not yet fully explored, we are justified in considering the *present* gas reserve to be something of the magnitude of 200 million million cubic feet.

"It is realized that this is a reserve of astronomical proportions. However, in my judgment, after thorough review of the data available on the 426 fields considered, this estimate will prove to be a conservative appraisal of the natural gas resources of the United States."

Canadian reserves, on the basis of limited data, appear to approximate 5-10 million million cubic feet. There appears to be no reason, then, to fear any immediate or even near-future shortage of natural gas, and this conclusion—strongly supported by testimony at recent hearings of the Federal Power Commission—is further substantiated by the fact that the Fischer-Tropsch process itself, using coal as a raw material, will apparently be able to produce a high-B.Th.U. "synthetic natural gas" which can compete economically (eventually, at least) with natural gas in regions remote from gas fields.

It is not at all impossible that, in the next decade or so, "synthetic natural gas" will be produced from coal in certain regions of the United States, by use of the Fischer-Tropsch process, while in other

regions, where natural gas itself is abundant and inexpensive, the Fischer-Tropsch process will continue to use natural gas as a process raw material. Transportation costs will hold the key to such a picture.

TABLE XXI

United States Natural Gas Resources *
(In Million Cubic Feet)

Gas-Producing States, by PAW Districts	*Recoverable Solution and Free Gas Reserve*	*Per Cent of U.S. Reserve*	*Estimated Gross 1945 Gas Production*
District 1			
Kentucky	——	——	90,000
New York	——	——	9,097
Ohio	——	——	61,500
Pennsylvania	——	——	95,361
West Virginia	——	——	200,000
Total District 1	4,930,000	3.42	455,958
District 2			
Illinois	237,500	0.17	49,000
Indiana	13,800	0.01	1,500
Kansas	13,955,339	9.67	171,000
Michigan	132,976	0.09	19,700
Oklahoma	6,771,172	4.69	370, 000
Total District 2	21,110,787	14.64	611,200
District 3			
Arkansas	968,416	0.67	48,000
Louisiana	13,964,303	9.68	730,000
Mississippi	1,358,404	0.94	7,900
New Mexico	1,965,250	1.36	135,400
Texas	85,773,478	59.44	2,636,908
Total District 3	104,029,851	72.09	3,558,208
District 4			
Colorado	333,600	0.23	4,206
Montana	590,800	0.41	32,492
Utah	74,679	0.05	6,651
Wyoming	664,400	0.46	46,384
Total District 4	1,663,479	1.15	89,733
District 5			
California	12,555,435	8.70	560,820
Grand total United States	144,289,552	100.00	5,275,919

* Calculated by E. DeGolyer on a pressure base of 16.4 pounds per square inch at 60° F.

Technical details on the synthesis of methane and other high-B.Th.U. gases by use of the Fischer-Tropsch process were discussed in Chapter 11, but it is pertinent here to note some figures recently released by P. C. Keith.[4] Discussing pilot plant work of Hydrocarbon Research, Inc., he states that "it appears certain that eventually a process will be developed whereby either coking or non-coking bituminous or anthractite coal can be completely gasified, yielding a pipe-line gas of approximately 1,000 B.Th.U. heating value. These preliminary studies further indicate that the net thermal efficiency, i.e., the ratio of the heating value of the product to the heating value of the coal, including all coal used as fuel, will be about 80 per cent. In other words, it is to be expected that one ton of 13,000-B.Th.U. coal will yield 20,000 cubic feet of synthesis gas."

In testimony before the Federal Power Commission, Keith further stated that his company has experimentally produced 500-900 B.Th.U. city gas from coal at an estimated cost of 17 cents per 1000 cubic feet. Further calculations on the production of 900-B.Th.U. gas from coal in a region such as West Virginia yield a cost of 19 cents per 1000 cubic feet, which, with added transportation costs, would amount to 24.2 cents at the city gate of New York.

While these figures may be somewhat "futuristic"—Alfred R.

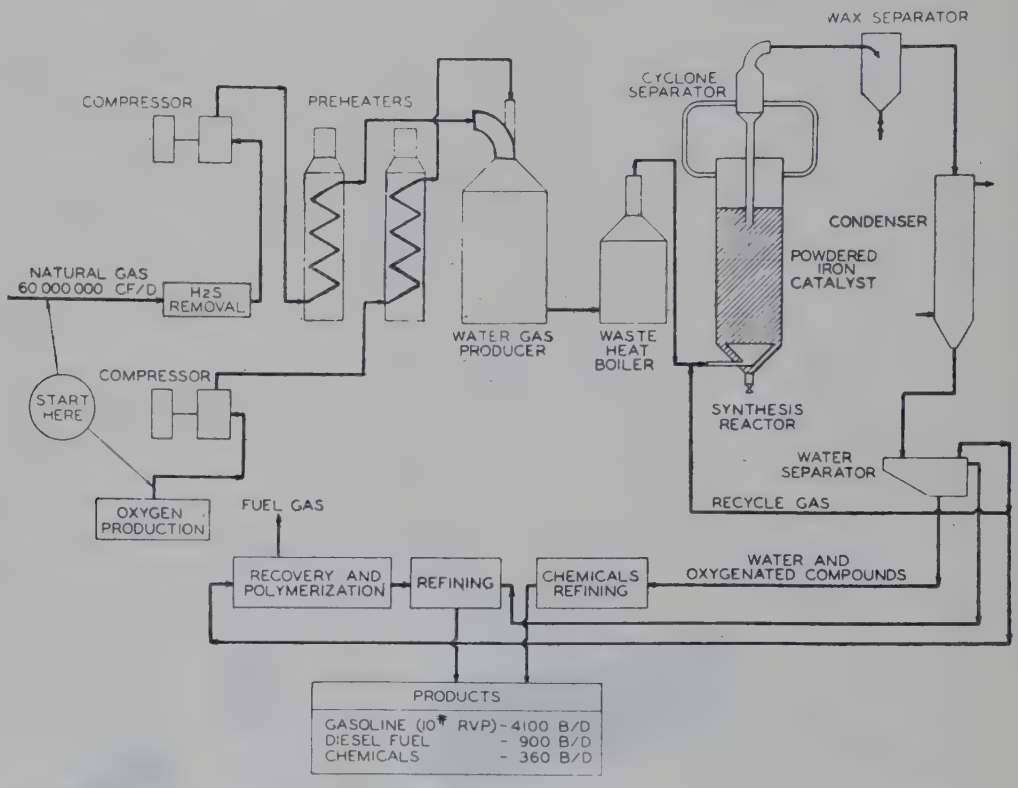

FIG. 18. *Flow diagram of the conversion of natural gas to motor fuel.*

Powell, associate research director of the Koppers Co., for one, took exception to them in later testimony before the Federal Power Commission,[2] and computations based on them indicate that they are somewhat out of line from a technical standpoint – it would appear that little fear need be felt that the use of natural gas in the Fischer-Tropsch process will be harmful to United States economy.

Yields from Natural Gas

As for coal, Fischer-Tropsch process yields from natural gas are dependent upon the process variations. Rough calculations are often based on the production of one barrel of gasoline per 11,000 cubic feet of natural gas (process material plus fuel). This figure probably introduces only minor errors, for it may be noted that Robert P. Russell has stated[1] that a European-design Fischer-Tropsch plant using natural gas as raw material would require 505 pounds (11,950 cubic feet) of natural gas per barrel of gasoline, while a plant of "possible future design" might require only 440 pounds (10,450 cubic feet).

Bruce K. Brown has stated[1] that the yield of "crude oil" is three to five gallons per 1000 cubic feet of natural gas (8,400-14,000 cubic feet of the latter per barrel of oil). *It should be noted, of course, that all the yield estimates for gasoline are based on the maximum production of that product by further refining (cracking, etc.) of the other primary products.* Where other products are desired, such as Diesel fuels, gasoline yields per 1000 cubic feet of natural gas are naturally lower.

It is interesting to note that P. C. Keith has commented[4] that "in the next several years, improvements in the Hydrocol process will make possible the production of a barrel of oil from 8,000 cubic feet of gas, including all gas used for fuel."

As regards commercial yields, reference may be made to the various chapters of Parts II and III and to the following examples.

According to Paul Ryan,[8] the Kellogg "Synthol" variant of the Fischer-Tropsch process will require approximately 11,000 cubic feet of natural gas to produce one barrel of liquid hydrocarbon product. This figure differs from the recent figure of "one barrel of crude synthetic oil ... for each 15,000 cubic feet of natural gas" to be charged to the proposed Stanolind plant which, it is said, will use the Synthol process; "substantial amounts" of oxygenated compounds will also be produced. No product breakdown was given by Ryan, but the Stanolind plant, according to report, will daily produce 6000 barrels of gasoline and 1000 barrels of distillate fuels from 100,000,000 cubic feet of dry natural gas.

P. C. Keith[4] reports that the Carthage Hydrocol, Inc., plant at Brownsville, Texas, "has been designed to process approximately 64,000,000 cubic feet of natural gas per operating day and to produce the following: motor fuel, 5,800 barrels per day; synthetic Diesel fuel, 1,200 barrels per day; and crude alcohols (in water solution), 150,000 pounds per day."

It may be noted that the proposed operation calls for the recovery of approximately 0.25 gallon of natural gasoline and butane per 1000 cubic feet of feed gas, so that this 381 barrels per day of motor fuel blending agents are presumably part of the plant's gasoline output. Including this, the Brownsville plant will have a gasoline yield of one barrel per 11,000 cubic feet of natural gas and a total hydrocarbon product yield of at least one barrel per 9150 cubic feet.

Both the Kellogg and Hydrocol figures are for gasoline of premium octane ratings and are, therefore, representative of modern processes.

Manpower Requirements

No data on this subject are immediately at hand, but it would appear that manpower requirements for natural gas production would be low—*far* lower than for coal mining—and that labour requirements for the "crude oil" and gasoline production steps might be somewhat lower than for Fischer-Tropsch operations using coal as the raw material.

There are obviously no sociological drawbacks to the process use of natural gas, other than those attendant upon its possible depletion. Serious as these might be, they are minimized by the possibility of "synthetic natural gas" production from coal.

Costs from Natural Gas

Most cost estimates have been based on the use of natural gas at five cents per 1000 cubic feet, a price at (or below) which vast quantities are at present (1946) obtainable in remote and newly-discovered fields. It is entirely possible, however, that Fischer-Tropsch process demands, coupled with normal expanding usage, will result in marked price increases, a significant factor when it is remembered that a plant, to pay out properly, ought to have assurance of a steady, stable-priced supply for at least ten years.

P. C. Keith has commented[4] that "the effects (on the natural gas industry) could be fundamental and far reaching. Firstly, the competition of natural gas with crude as a source of gasoline is certain to increase the price of gas at the well head. In the next several years, improvements in the Hydrocol process will make possible the production of a barrel of oil from 8,000 cubic feet of gas,

including all gas used for fuel. If at that time the capital and operating cost of a Hydrocol plant is on a par with an oil refinery (and there is no basic reason why this cannot become true), then 8,000 cubic feet of gas at the refinery will be the equivalent of a barrel of 30° API gravity Mid-Continent crude. Then, under these conditions, gas at 17 cents per 1000 cubic feet just balances crude oil at $1.35 per barrel; both prices as delivered to the refinery.

"It is the author's guess that gas in such localities as Hugoton, East Texas, and the Gulf Coast will never quite reach the equivalent price of crude oil. In the first place, gas transportation is inherently more expensive than the transportation of crude oil. Secondly, gas must always be transported by gas pipe line and not by tank cars.* Therefore, its mobility is limited. Thirdly, the effect which the actuality of cheap oxygen will have upon manufactured-gas costs will tend to limit the competitive value of natural gas for pipe lines. Nevertheless, gas prices will go up. It is not unlikely that, in the localities just mentioned, gas at the well head will be worth 10-12 cents (per 1000 cubic feet) within the next decade."

Much of the published data on costs are obsolete because of technical process advances, but they may be interpreted as setting a ceiling on present-day figures. According to Robert P. Russell[1] European-design Fischer-Tropsch plants, using natural gas costing five cents per 1000 cubic feet, would produce gasoline at a cost of 8.8 cents per gallon, including depreciation. A plant of "possible future design" according to this 1943 estimate, would yield gasoline at a total cost (including depreciation) of 4.8 cents per gallon.

These figures conflict sharply with an estimate made by Fred Denig,[1] based on a smaller plant of European design (using natural gas); this estimate was 17.4 cents per gallon of gasoline, but Mr Denig testified that it could be lowered by future developments.

It is pertinent here to turn again to the recent announcements concerning commercial Fischer-Tropsch process variants. According to Paul Ryan,[8] the Kellogg "Synthol" process can "produce motor gasoline (75 clear octane CFRM) for approximately five cents per gallon (including 10 per cent depreciation) from natural gas valued at five cents per 1000 cubic feet."

Very similar figures are reported for the Hydrocol process; P. C. Keith[4] states that "the finished gasoline produced by Hydrocol with a Reid vapour pressure of 10 pounds has a clear octane number of 80 Motor Method or 88-90 Research. ... The Diesel oil has a

* It was rumoured in 1944 [9] that plans were under way looking to the post-war construction of tankers to ship liquefied natural gas from the Gulf coast to eastern population centres.

gravity of about 38° API, a cetane number of 45-50, and a pour point below 0° F. The oxygenated compounds in water solution consist mainly of acetaldehyde, acetone, and ethyl, propyl, butyl, amyl, and heavier alcohols. This last product offers an extremely attractive source of chemical raw materials. ...

"Allowing credit for the Diesel oil at 3.5 cents per gallon and for the crude alcohols at 0.5 cent per pound, it is predicted that the 'out-of-pocket' cost of the gasoline will run about 2.5 cents per gallon. This cost includes all expenses and charges exclusive of capital costs. When capital costs, including interest, depreciation, and amortization are added, the cost of the gasoline becomes 5.25 cents per gallon."

E. V. Murphree, who certainly is in an informed position, recently told the American Gas Association that the production of synthetic gasoline from natural gas via the fluid catalyst Fischer-Tropsch process now appears directly competitive with gasoline from crude oil.[6] Although the cost of producing gasoline from natural gas may be even slightly lower than the cost of obtaining it from crude oil, the plant investment in the former case is "substantially higher," Murphree stated.

Incidentally, G. G. Oberfell pointed out in early 1946[7] that "modifications of the Fischer-Tropsch process, using natural gas, undoubtedly will find useful applications, particularly where the process can be combined with other processes or with existing facilities. The production of natural gasoline and the manufacture of chemicals afford opportunities for such combinations. However, without the economic advantages of such combinations, the available information indicates that as a means of producing gasoline alone the Fischer-Tropsch process would not be competitive with present refinery operations, using crude oil as a raw material, under present prices. ...

"On the basis of conservative published estimates, the synthesis process utilizing natural gas will not be able to compete with present refinery methods utilizing crude petroleum until the price of crude reaches about $1.75 to $2.00 per barrel. On the basis of experimental data not yet confirmed by large-scale commercial operations, gas may be competitive with crude oil under special circumstances."

It is certainly wise to observe caution in extrapolating data for plants which assign even reasonable values to oxygenated hydrocarbon by-products to cover a whole industry, for chemical markets are strictly limited, even if rapidly expanding, and a vast flood of Fischer-Tropsch by-product chemicals might result in chaos and losses for all, including Fischer-Tropsch plant operators.

It would not be surprising if many refiners ignore by-product potentialities in their first economic appraisal of a Fischer-Tropsch process variant. In many cases, oxygenated hydrocarbons, if produced in large quantities, may have to be converted to hydrocarbon products by cracking or hydrogenation, or used directly as fuel blending agents. This situation would be analogous to the present refinery production of gasoline by polymerization of mixed olefinic gases; such gases have diverse chemical uses, but some of them are available in far greater quantities than chemical markets could absorb.

In any case, cost estimates indicate that the Fischer-Tropsch process, using natural gas, is ready—or nearly ready—to compete with the use of crude oil for the production of gasoline and other petroleum products. Actual costs for large-scale operations will soon be determined in some of the recently announced plants, which will be discussed later, and by the five-year research programme of the U.S. Bureau of Mines.

Investment Required

Robert P. Russell stated in 1943[1] that the investment required for the daily production of 100,000 barrels of synthetic gasoline from natural gas would range from $220,000,000 (for a plant of "possible future design") to $477,000,000 (for a plant of European design). These figures are not very much higher than the investment figures for petroleum refining and production, although they do not include any investment figure for natural gas fields.

Paul Ryan, in his article on the Kellogg "Synthol" process,[8] mentions that "a complete Synthol plant to produce a large volume of liquid hydrocarbons, it is presently estimated, would have a 'payout time' of approximately eight years. A combined Synthol and chemical plant, it is presently estimated, would have a payout time of approximately three years. This acceleration in financial return is due to increased values of the chemical compounds over the values of the hydrocarbons," but it should again be noted that not too many plants could benefit in this way.

More details have been published on the investment required for the Hydrocol process. The plant at Brownsville, Texas, which will produce 5800 barrels per day of motor fuel, 1200 barrels daily of synthetic Diesel oil, and 150,000 pounds per day of crude alcohols, will cost an estimated $15,000,000. On the basis of the gasoline alone (obviously an unfair one), this amounts to an investment cost of about $2,600 per daily barrel. Extrapolated to a production figure of 100,000 barrels per day (again obviously unfair, since mass production economics would presumably be involved), this Fischer-Tropsch

variant would require an investment of $260,000,000, a very reasonable figure when it again is realized that no investment allowance has been made for the Diesel oil and chemicals.

P. C. Keith, in his comments on this investment and on product costs,[4] remarks that, "discounting any advantages which would result from a probable increase in the price of crude, it is obvious that the most fruitful avenue for improvement in the economics of the process is in the reduction of capital cost. Substantial reductions in the cost of future Hydrocol plants seem probable."

Steel Requirements

No data are at hand on recently announced processes, but Robert P. Russell testified in 1943[1] that a Fischer-Tropsch plant of European design (using natural gas) would require 6.5 tons of steel per daily barrel of gasoline, while one of "possible future design" would require only 2.8 tons of steel per daily barrel. For the daily production of 100,000 barrels of gasoline, therefore, some 280,000 to 650,000 tons of steel would be required for construction purposes.

These figures are comparable to those for petroleum refining and are lower than those generally reported for Fischer-Tropsch plants using coal as raw material. They are still sufficiently high, however, to indicate that no large industry could be rapidly constructed in an emergency. For example, some 2,800,000 tons of steel would be required were the Fischer-Tropsch process, at some hypothetical time, to be suddenly called upon to supply 1,000,000 barrels of gasoline per day to replace an equivalent amount of imports cut off by war; this figure is over 3 per cent of recent U.S. wartime steel capacity and represents fabricated parts, not raw steel. The implications are obvious.

Efficiency Calculations

Conservation of natural fuel resources, while not now as critical as before the advent of atomic (nuclear) energy, still requires that every process be analyzed as to its fuel efficiency—even if this analysis is promptly disregarded for other reasons.

Basing his calculations on data released by Robert P. Russell,[1] G. G. Oberfell has recently published[7] some interesting information on this subject; some of this is shown in Table XXII.

As Oberfell points out, "from 1000 cubic feet of methane, allowing none for fuel requirements, it is theoretically possible to obtain about 6.5 gallons of motor fuel. The fuel value of this 6.5 gallons of motor fuel would be about 75 per cent of the fuel value of the original 1000 cubic feet of methane. Therefore, the maximum fuel

value recoverable is about 75 per cent. In practice, however, even with 100 per cent reaction efficiency as above, some methane will be required for fuel purposes. Consequently, yields will always be less than 75 per cent of the fuel value of the methane used to produce it. Improved reaction efficiencies and, particularly, improved techniques of synthesis gas production will no doubt reduce the amount of gas required, with the result that net yields as high as 4.5 to 5.0 gallons per 1000 cubic feet may be obtained in large-scale operations.

"For every cent of cost per 1000 cubic feet of methane with 50 per cent of the fuel value converted to gasoline, the raw material cost alone will be $\frac{1}{4}$ cent per gallon of gasoline."

TABLE XXII

Efficiencies of Gasoline Production by the Fischer-Tropsch Process [7]

Raw Material	*Raw Material to Produce One Barrel of Gasoline*	*Therms Necessary to Produce One Barrel of Gasoline*	*Therms Contained in One Barrel of Gasoline*	*Percentage of Fuel Value of Raw Material Converted to Gasoline*
Coal	1,360 lb.	163.0	50.5	31.0
Methane (European Design)	505 lb. (11,950 cu. ft.)	119.0	50.5	42.3
Methane (Possible Future Design)	440 lb (10,450 cu. ft.)	104.5	50.5	48.3

In regard to the low efficiency shown in Table XXII for the conversion of coal, two facts, should be noted. First of all, much less coal per barrel of gasoline is required for modern processes (continuous gasification), raising the efficiency figure to a level comparable to that for natural gas.

Secondly, the normal use of coal in a steam locomotive involves a thermal efficiency of only about five per cent, while the use of gasoline or Diesel oil in an automobile or Diesel locomotive results in thermal efficiencies of about 25 per cent. Assuming that 5.27 pounds of coal are required per pound of gasoline produced (the figure for the obsolete process shown in Table XXII); that the bituminous coal has a heating value of 12,500 B.Th.U. per pound; and that the heating value of the gasoline or Diesel fuel is about 19,000 B.Th.U. per pound, the following situation prevails:

$$5.27 \times 12{,}500 \times 0.05 = 3{,}290 \text{ B.Th.U.}$$
$$19{,}000 \times 0.25 = 4{,}750 \text{ B.Th.U.}$$

$$\text{Comparative Efficiency} = \frac{4{,}750}{3{,}290} \times 100 = 144 \text{ per cent}$$

The potential railway use of steam- and gas-turbine, coal-fired, locomotives will somewhat invalidate this striking comparison, but it is nevertheless highly pertinent to the situation as it exists today. Keith, moreover, has recently[5] emphasized this point by stating that "both gas and oil are more efficient fuels than coal. While very large high-pressure, high-temperature steam stations may achieve a thermal efficiency of 31 per cent, a better average figure would be 28 per cent. On the other hand, Diesels or high M. E. P. gas engines can, even in small sizes, achieve an efficiency of 34 per cent." However, he goes on to state (and substantiate by statistics) that "until the capital and operating costs of converting coal to oil can be decreased, oil from coal will not compete with coal as an industrial fuel," but "gasoline made from coal will in the near future compete with gasoline made from crude ... and there is impending competition between coal moved as gas and coal moved as-is."

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Chapter 20

THE CURRENT SITUATION

MANY if not all of these economic and technical factors have received attention, in recent years, from a number of petroleum companies, from the coal industry, from government bureaux and research agencies, and from regional and college research groups in the United States. The competitive nature of the United States' industrial pattern has, of course, made it necessary for many of these organizations to release little information on their activities, but enough has been revealed to show that widespread, intensive research is under way on many phases of the Fischer-Tropsch process.

The projected construction of several commercial Fischer-Tropsch plants has already been announced. The first of these, that of Carthage Hydrocol, Inc., will be erected near Brownsville, Texas, at a cost of about $15,000,000.

Carthage Hydrocol, Inc.

This plant, it is said, will use natural gas in a process developed by P. C. Keith of Hydrocarbon Research, Inc. Construction and operation of the plant will be financed by eight companies with the aid of a $9,000,000 loan from the Reconstruction Finance Corporation.

The eight companies involved, together with their capital investments are as follows: The Texas Company, $3,778,125; Forest Oil Corp., $1,259,375; Niagara Share Corp., $1,259,375; United Gas Corp., $1,007,500; La Gloria Corp., $1,007,500; Gulf States Oil Company, $377,812; Stone & Webster, Inc., $377,812; and the Chicago Corp., $503,750. It will be noted that the capital stock amounts to nearly $10,000,000; it is said that The Texas Company, the largest stockholder, is to have first consideration as a purchaser of the plant's products, especially the "premium gasoline ... for use as a sweetener for low grade gasoline."

Construction of the plant will be under the direction of Hydrocarbon Research, Inc., which controls the patent rights; these, it is said are being supplied to Carthage Hydrocol royalty free. Pilot-plant (10 gallons per day) and demonstration-plant (10 barrels per day) phases of the work, it is reported, were carried out at Olean, New York, and were backed, to the extent of $1,250,000, by the

Magnolia Petroleum Company, the La Gloria Corp., and the J. S. Abercrombie Company. Another report mentions a larger experimental plant at Montebello, California, and states that "later material development and engineering contributions were made by the Standard Oil Company of New Jersey and by the Texas Company."

As previously mentioned, the plant will produce 5800 barrels per day of motor fuel with a clear octane number of 80 Motor Method or 88-90 Research and a Reid vapour pressure of 10 pounds; 1200 barrels daily of 38° API synthetic Diesel oil with a cetane number of 45-50 and a pour point below 0° F.; and 1200 barrels per day of crude alcohols (in water solution), these oxygenated compounds consisting chiefly of acetaldehyde, acetone, and ethyl, propyl, butyl, amyl, and heavier alcohols. Some 64,000,000 cubic feet of natural gas will be used per day.

The process in question involves:

(1) Recovery of 0.25 gallon of natural gas and butane per 1000 cubic feet of feed gas;

(2) Separation from the air, by compression to 75 pounds per square inch, of 40,000,000 cubic feet per day of high-purity oxygen at a cost of 4.8 cents per 1000 cubic feet, based on a plant investment of $3,500,000 and amortization at 12.5 per cent per year, but with no charge for power and water, since both are available as process by-products from the exothermic synthesis reaction;

(3) The partial combustion of 64,000,000 cubic feet of natural gas daily with the high-purity oxygen, yielding the required synthesis gas mixture of carbon monoxide and hydrogen;

(4) The conversion of this synthesis gas at 250 pounds per square inch, using a "cheap, rugged, iron-base catalyst," in finely-divided form, which is circulated by the fluid-catalyst technique;

(5) The separation of the Fischer-Tropsch products by fractionation and absorption processes;

(6) "Treatment of the gasoline to remove oxygenated compounds, polymerization of the propylene and butylene, re-running, blending, etc., and,

(7) "The manufacture and revivification of the catalysts."

All of the information sources on this plant[4, 8, 12, 17, 18, 20] do not agree in every detail, but the foregoing summary includes the data which appear to be determined. Construction of the plant was scheduled to begin in March 1947, and to be completed early in 1948.

Stanolind Oil and Gas Company

According to recent announcements engineering work is now in progress for the construction of a Fischer-Tropsch plant in the south-western Kansas sector of the Hugoton gas field by the Stanolind Oil and Gas Company. Some 100,000,000 cubic feet of natural gas per day is to be used in the "Synthol" process to produce 6000 barrels per day of gasoline and 1000 barrels per day of distillate fuels, the products to be marketed in the Kansas area.

The exact location of the plant has not been announced; it was reported in 1946[16] that this would not be decided until after more study of the transportation problems involved and that "completion of the proposed plant may be delayed as long as two years, because of the difficulty in obtaining materials."

Stanolind states that it has been conducting research for several years, at its Tulsa laboratories, on variations of the German Fischer-Tropsch processes, adapting these to natural gas and oxygen as raw materials, and employing fluid catalyst techniques. Recent announcements mention that a "special powdered-iron catalyst" will be employed in "large 'fluid' type reactors." In the production of the synthesis gas, low-heating-value natural gas is to be "burned under 300 pounds pressure with relatively pure oxygen," which latter material will be "produced by fractionating liquid air in the largest plant ever constructed for this purpose."

"For each 15,000 cubic feet of gas charged to the plant, one barrel of crude synthetic oil and substantial amounts of oxygenated compounds (including alcohols, ketones, aldehydes, and acids) are produced. The recovery and treatment of the hydrocarbon products for market would be accomplished by conventional refinery methods."

Other than the repeated statement that the "Synthol" process will be employed, no further technical details have been released so far.

Humble Oil & Refining Company

In the light of the previously quoted statements of E. V. Murphree, it is not particularly surprising that Humble Oil & Refining Company an affiliate of the Standard Oil Company (New Jersey) group, has recently announced[15] that it "is considering building a plant to utilize natural gas similar to the new Hydrocol plant at Brownsville." If and when built, the plant will probably be located on the Gulf Coast, it was said.

M. W. Kellogg Company

This company's "Synthol" process has been discussed in several places in this book and, as mentioned previously, will be used in the

Fischer-Tropsch plant planned by the Stanolind Oil and Gas Company.

According to the available information, the Kellogg "Synthol" process is capable of producing 75 ASTM octane number (83 Research) gasoline for about five cents per gallon, using natural gas at five cents per 1000 cubic feet and figuring plant depreciation at ten per cent per year. According to Kellogg claims,[22] the major product of the process (produced in 80 per cent yield, presumably based on the primary products) consists of the aforementioned gasoline, which can be leaded to 80 ASTM octane number by the addition of one cubic centimetre of tetraethyllead.

No process details have been released, but reference to recent information on Stanolind's plant would seem to indicate marked similarities to the "Hydrocol" and other processes—use of relatively pure oxygen for partial combustion of air in the synthesis gas production, use of the fluid catalyst technique, use of powdered iron catalysts, etc. Kellogg has long been interested in and engaged in research on the Fischer-Tropsch (or "Synthol") process, so that it is entirely likely that it will construct more than the Stanolind plant in the next few years.

Standard Oil Company of New Jersey

The exact position of Jersey Standard in the Fischer-Tropsch field is not completely clear, although Humble Refining's recent announcement of a contemplated Fischer-Tropsch plant indicates that the mother company intends to be more than a process licensor. In addition, Jersey Standard has made "material development and engineering contributions" to the Hydrocol Process, and it is known to have extensive patent interests in this field, many of these acquired from the I. G. Farbenindustrie A.-G. and presumably to be returned to Jersey Standard by the Alien Property Custodian in accordance with the recent decree of a United States District Court.

Late in 1943, Jersey Standard was granted priorities to construct a Fischer-Tropsch pilot plant, which was completed in July, 1945, at Baton Rouge, Louisiana.[4] In view of the company's extensive research in this field, its many economic releases, its patent holdings, and the recent Humble Refining announcement, it is certain that more will be heard concerning its future activities.

It is interesting to note, incidentally, that the Pittsburgh Consolidation Coal Company is reported[9] to be "planning to join the Standard Oil Development Company in the inauguration of a major, privately-financed research programme to investigate the carbonization and complete gasification of coal." It is said the Standard will

contribute its petroleum "know-how" and that Pittsburgh Consolidation will broaden its research activities at its plant in Pennsylvania.

Mergers similar to this will be viewed with interest, since they indicate co-operation instead of competition as regards the production of synthetic fuels from coal. The petroleum industry possesses a valuable back-log of refining knowledge, process patent rights, and—most essential—marketing experience in and retail outlets for the sale of "petroleum" products, so that co-operation from the coal industry, which possesses the ultimate raw material for Fischer-Tropsch operations, is a logical step, whether or not it will be uniformly followed.

Standard Oil Company (Indiana)

One of the few indications of Indiana Standard's direct activity in this field, other than the several related patents which have issued to it, is the statement in its 1944 annual report that, "while the company has no fear of the early exhaustion of crude supplies, it is already at work on methods for the possible future production of motor fuels from natural gas and coal."

Robert E. Wilson, chairman of the board of Standard of Indiana, has been the author of a number of papers[23] on this and related petroleum substitute topics, and it was recently revealed that his company is considering "the adaptation to Standard's Whiting (Indiana) plant of the German 'OXO' technique for making higher-boiling alcohols used in many industrial processes."[7]

It must also be remembered that Standard of Indiana is the parent company of Stanolind, so that the latter's projected plant may be interpreted as more than an academic interest on the part of the mother company.

The Texas Company

Prior to its assumption of the leading role in the projected Brownsville, Texas, plant of Carthage Hydrocol, Inc., The Texas Company is known to have constructed a Fischer-Tropsch pilot plant at its Los Angeles, California, refinery, at an estimated cost of $880,827;[1] a later report[4] stated that the company expected to finish its pilot plant "near Wilmington, California," about October 1, 1945. This pilot plant may also be the pilot plant "at Montebello, California," which "has shown that the (Hydrocol) reaction goes smoothly and controllably."[18]

Champlin Refining Company

While nothing further has been published about it since 1944, it was reported in September of that year that Fred C. Koch, a consult-

ing engineer, had leased 100,000 acres of land in the Hugoton field (Kansas and Oklahoma) in anticipation of erecting a Fischer-Tropsch plant to use natural gas as raw material. The Champlin Refining Company had "tentatively agreed to go into the project," according to this statement.[2]

Later information indicated that Koch felt that his plans had been given "a great deal more attention than they warrant." Although he eventually intends to utilize the leased acreage for a Fischer-Tropsch plant, Koch pointed out that much in the way of experimental work and financing remained to be done before construction could be undertaken. "It is definitely a long-range proposition and is nothing to get excited about for the present," he said.[19]

Petroleum Hydrocarbons, Inc.

A $12,000,000 Fischer-Tropsch project (half to be privately financed) was reported[3] pending before the Reconstruction Finance Corporation in October, 1944. The proposal was made by Petroleum Hydrocarbons, Inc., which planned to use natural gas from the Hugoton field of Kansas. No further idenitificaton of the principals of Petroleum Hydrocarbons, Inc., has appeared in the literature, nor has anything further been written about this project.

Government Research

The Government of the United States is vitally interested in the availability of future supplies of petroleum, and it was for this reason that Congress passed, in 1944, a bill authorizing the expenditure of $30,000,000 over a five-year period for research on synthetic liquid fuels—on coal hydrogenation, shale oil production, the Fischer-Tropsch process, and the manufacture of oxygenated hydrocarbon fuels from agricultural waste materials.

Few concrete details on the work of the Bureau of Mines (the agency assigned to conduct this research) have so far been generally published, but this is to be expected, since the first few years have been devoted to plant design and construction and to planning.

In a speech given in September, 1944, before the American Chemical Society, H. H. Storch revealed that the Bureau planned to use $2,500,000 out of the $5,000,000 allotted to it by Congress for the first year of the project for the erection of a research and development laboratory at Bruceton, Pennsylvania (near Pittsburgh), for process development on the Fischer-Tropsch and coal hydrogenation processes.

Later in the year, the Bureau established an Office of Synthetic

Liquid Fuels, headed by W. C. Schroeder, to function as part of the Bureau's Fuels and Explosives Branch. Three of the new Office's divisions are concerned in some manner with the Fischer-Tropsch process: Research and Development, headed by H. H. Storch; Synthesis Gas Production, headed by W. W. Odell; and Gas Synthesis Demonstration plant, whose chief was not announced at that time.

In its request to Congress for funds for 1945-46, the Interior Department revealed that a Fischer-Tropsch pilot plant of 10 barrels per day gasoline capacity was planned for completion at Bruceton by the fall of 1945 and that, after this plant had served its purpose, a 200-barrel-per-day plant would be constructed.

This latter plant, presumably, involved the conversion of equipment at the Missouri Ordnance Works at Louisiana, Missouri, a plant controlled by the Army Ordnance Department and built during the war, at a cost of $17,000,000-$19,000,000 for the synthesis of ammonia from natural gas. A coal hydrogenation unit was to be constructed first at this plant, incidentally.

It appears, however, that the War Department has ordered this plant to be returned to the production of ammonia for the duration of the world food emergency. It was conceded that this step would delay the Bureau of Mines' project, but design work will continue as will "certain construction activity"; part of the plant may be available.

In the fall of 1945, the establishment of a new laboratory and research unit on the campus of West Virginia University at Morgantown, West Virginia, was announced[5] as a co-operative project between the Bureau of Mines and the University, in which the Bureau would initiate a research programme involving about $100,000 per year. The University "will conduct experiments in the production of gases required in the manufacture of synthetic liquid fuels from coal."

Early in 1946, the Bureau signed a contract with the Girdler Corporation to construct a $249,000 plant to produce 110,000 cubic feet of hydrogen and 120,000 cubic feet of synthesis gas daily, the plant to be erected at the Bureau's Bruceton, Pennsylvania, synthetic liquid fuels laboratory.

Table XXIII shows the budgeted expenditures of the Bureau of Mines for synthetic liquid fuels research, as submitted to Congress, early in 1947, for the fiscal year 1948.

The Bureau of Mines has been more than actively interested in experiments on the campus of the University of North Dakota, at Grand Forks, on the gasification of lignite to produce either a

TABLE XXIII

Budgeted Expenditures of Bureau of Mines for Work on Synthetic Liquid Fuels*

Project	*Estimate* 1948	*Estimate* 1947	*Actual* 1946	*Actual* 1945	*Accumulated Total*
Hydrogenation and Gas Synthesis, Research and Development	$1,500,000	$1,856,140	$2,469,765	$1,571,969	$7,397,874
Hydrogenation Demonstration Plant	3,000,000	4,200,385	1,606,595	—	8,806,980
Synthesis:					
Research on Gas Production....	275,000	250,000	140,000	36,810	701,810
Demonstration Plant	500,000	1,042,000	—	—	1,542,000
Oil Shale:					
Research and Development	375,000	393,514	255,000	585,000	1,608,514
Mining	350,000	335,000	325,000	32,355	1,042,355
Demonstration Plant	1,000,000	1,000,000	780,000	370,467	3,150,467
Total Obligations	$7,000,000	$9,077,039	5,576,360	$2,596,601	$24,250,000
Anticipated Obligations**		410,000	—	—	—
1945 Balance Available in 1946 ..			−2,403,399	+2,403,399	
1946 Balance Available in 1947 ..		−3,827,039	+3,827,039		
Total Estimate or Appropriation ..	$5,000,000	$5,250,000	$7,000,000	$5,000,000	$22,250,000

* As contained in the Federal Budgets for the fiscal years 1947 and 1948.

** Sum transferred in 1945 to the Department of Agriculture (but not yet obligated) for work on the production of synthetic liquid fuels from agricultural and forest products, as provided in the Synthetic Liquid Fuels Act.

hydrogen-rich gas for iron ore reduction or a synthesis gas for such operations as the Fischer-Tropsch process. As previously mentioned, lignite is quite inexpensive, "costing not more than $1.25 a ton at the mine,"[6] so that such gas might be made fairly cheaply.

"Yields of 33,000 cubic feet of 300 B.Th.U. gas per ton have been attained (in a satisfactory initial run). Ratios of hydrogen to carbon monoxide can be varied from 1.2 to 12. Higher ratios are obtained at lower temperatures."[21]

It was reported in 1945[6] that the commerical-sized Parry retort at Grand Forks cost $125,000 and has a capacity of 400,000 cubic feet of gas per day; this type of retort was initially developed by the Bureau of Mines at Golden, Colorado. "It can produce a gas which is raw material for conversion to liquid fuels through the Fischer-Tropsch process, with a yield as high as 50 gallons (1.19 barrels) from a ton of sub-bituminous coal, besides naphtha, kerosene, and other by-products." In this plant, the lignite is fed from a hopper into the 60-foot retort, giving up its moisture and thus "self-steaming" itself. As the lignite then passes further down the annular chamber inside the reaction tube, it is mixed with superheated steam (at 1000-2000° F.), the steam entering from a recuperator adjacent to the retort shell, and thus is further gasified.

In the spring of 1946, the Bureau of Mines named a technical industry advisory committee to serve as a consultant to and receiver of information from its synthetic liquid fuels research programme. Committee members include: Eugene Ayres, chief chemist, Gulf Research & Development Company; H. W. Field, assistant manager, research and development department, Atlantic Refining Company; Louis S. Kassel, research engineer, Universal Oil Products Company; P. C. Keith, president, Hydrocarbon Research, Inc.; L. C. Kemp, Jr., director of research, The Texas Company; E. V. Murphree, vice-president in charge of research, Standard Oil Development Company; J. K. Roberts, research director, Standard Oil Company of Indiana; and H. Rubin, M. W. Kellogg Company. Also on the committee are George Creel, research engineer, Pittsburgh Consolidation Coal Company; Fred Denig, research director, Koppers Company; and Harold J. Rose, research director, Bituminous Coal Research, Inc.

The recent "Report of the Secretary of the Interior on the Synthetic Liquid Fuels Act from January 1, 1946, to December 31, 1946," reveals that a very active research programme is under way. The Research and Development Division has engaged in "experimental plant scale" research on "a new type of synthesis chamber which controls the catalyst temperature by dripping a cooling oil

directly over the catalyst," permitting "production rates in excess of twice (perhaps 3-5 times) those achieved in European practice." Chambers of this type may be "enlarged to any size which is practical from a construction standpoint; ... very much less steel is used per barrel of oil per day than in the Ruhrchemie process, and it (the new process) shows promise of equalling in industrial applicability the fluidized catalyst process recently developed by American oil company engineers."

Several exploratory laboratory-scale experiments were also under investigation in 1946, including work on a liquid-phase catalyst suspension process, a hot-gas recycle process, and fluidized fixed-bed processes designed to produce "a larger fraction of Diesel oil than is possible with the fluid-flow process recently developed by oil industry engineers."

In addition, the Research and Development Division is: (1) conducting laboratory investigations on the Fischer-Tropsch process mechanism (to provide data for rational design of pilot plants), (2) continuing an extensive catalyst testing programme, (3) carrying on studies of the physics of the heat transfer involved in the synthesis steps, and (4) preparing comprehensive patent and technical literature reviews. The new Research and Development Plant at Bruceton, Pennsylvania, was scheduled for early-1947 completion, and 1947 research "will be several times the amount that could be carried out with the limited equipment available in 1946."

The Synthesis Gas Production Division, with headquarters at Morgantown, West Virginia, engaged in building remodelling work (in a building provided by West Virginia University) in 1946, and conducted a study of the "Usefulness of American Coals in Gas-Making Processes." As mentioned earlier in this book, this division of the Office of Synthetic Liquid Fuels is co-operating with the Alabama Power Company in underground coal gasification experiments. It is also engaged (through a Pulverized Fuel Gasification Section) in "investigation of both foreign and domestic gas-making methods"; following a critical study, a "decision was made to concentrate on the development of pulverized fuel gasification in internally-heated reaction chambers similar to the Wintershall-Schmalfeldt process used successfully in Germany." The Mechanical Engineering Section is concentrating on concurrent problems "pertaining to the production and storage of (low-cost) oxygen," and a Gas Treating and Testing Section is working on purification problems.

The research programme of the Bureau of Mines is undoubtedly the most comprehensive study being made at present on the Fischer-

Tropsch process. Rightly, its efforts are concentrated on the use of coal as the process material; the Bureau is said to feel that natural gas phases are being adequately studied by the petroleum industry and that coal, in any case, is the ultimate raw material for large-scale use. While certain individuals have derided the term "demonstration programme," much used by the Bureau in its testimony to Congress before the inception of the present programme, there is little doubt that valuable process and economic data will result from this programme.

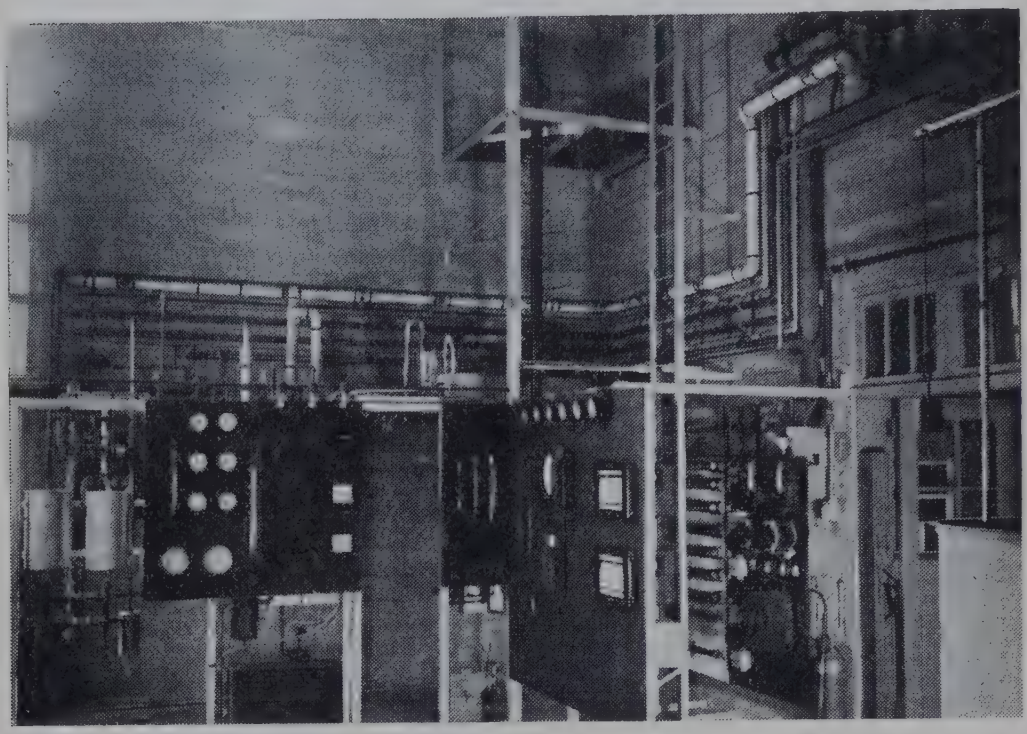

FIG. 19. *Internally-cooled, experimental Fischer-Tropsch plant of Bureau of Mines.* (Courtesy of H. H. Storch, U.S. Bureau of Mines.)

The Bureau had conducted preliminary research on the Fischer-Tropsch process for a number of years before the present programme, and it is not likely that this work will terminate at the end of the present five-year period. In fact, legislation was introduced in Congress, early in 1947, to increase the $30,000,000 limit to a figure of $60,000,000 and to extend the time limit to a total of eight years from the present five. Further, if Congress adopts this programme, the Office of Synthetic Liquid Fuels plans to put increased emphasis on research on the Fischer-Tropsch process. Government research may not always have the objective approach of industrial research, but it can often render invaluable service.

The United States Navy, incidentally, is very interested in high-quality Fischer-Tropsch Diesel fuels to power its multiplicity of Diesel-engined ships. It is not unlikely, also, that both Armed Services of the United States will inquire into the utility of Fischer-Tropsch distillates for jet-propelled and gas turbine planes. Co-operation between Government and industry in the Fischer-Tropsch research field is likely to yield results of value to all.

Other Organizations

It has recently been reported[13] that a Calgary (Canada) oil company is planning to erect a $100,000 pilot plant, capable of handling 2,000,000 cubic feet of natural gas per day and of producing five gallons of gasoline per 1000 cubic feet (a very high yield, if true).

Many other petroleum companies are engaged in research on the Fischer-Tropsch process but have as yet made little mention of their findings. Certain coal companies are also active in this field, and Table XXIV, prepared in early 1945, gives a qualitative picture of interest as it is measured by patent ownership.

The Office of the Alien Property Custodian represents an indeterminate factor in this field. At one time, it claimed about 200 patents —nearly a third of all that had been issued at the time—but a list issued early in 1946 contained the numbers of only 20 patents and 14 patent applications, so that the Federal Court ruling *re* Standard of New Jersey has vitally affected its position as a non-exclusive licensor of important Fischer-Tropsch patents. Nevertheless, many of its patents are of considerable significance.

Countless other organizations are interested in this field. The Institute of Gas Technology, for example, is engaged in a search for active, sulphur-resistant catalysts suitable for the production of specific products (the study attacks these desirable features separately, as well), with the intent of producing gas-enrichment hydrocarbons, possibly in standby or seasonably-idle water gas facilities. Bituminous Coal Research, Inc., announced in 1944 that its $2,500,000 five-year research programme on the utilization of coal would include a study of direct gasification.

All of this activity—technical and economic—is indicative of the present and potential importance of the Fischer-Tropsch process.

This book has not dealt at all with the economics of Fischer-Tropsch-intermediate-derived lubricants and chemicals, since it is obvious that Fischer-Tropsch gasoline is of chief immediate concern, but the data in Part III are testimony to the fact that "OXO" alcohols, by-product oxygenated hydrocarbons, and possibly a few detergents and synthetic fatty acids are likely to appear on the scene in the

TABLE XXIV

Number and Type of United States Patents on the Fischer-Tropsch Process or Related Syntheses Possessed By Companies Holding at Least Five Such Patents*

SUBJECT COVERED BY UNITED STATES PATENTS

COMPANY	Preparation of Synthesis Gas			Catalytic		Catalysts			Apparatus				TOTAL
	From Hydrocarbons & Steam, Etc.	From Water Gas	Purification	To Hydrocarbons	To Oxygenated Compounds	For Synthesis Gas Production	For Hydrocarbon Production	For Oxygenated Compounds Production	For Synthesis Gas: By Methane-Steam Reaction	For Synthesis Gas: By Water-Gas Reaction	For Catalytic Synthesis: To Hydrocarbons	For Catalytic Synthesis: To Oxygenated Compounds	
Amercan Lurgi Corporation	—	—	—	5	—	—	—	—	—	—	—	—	5
Atmospheric Nitrogen Company	5	—	—	—	—	—	—	—	—	—	—	—	5
Badische Anilin & Soda Fabrik	1	1	—	2	4	—	—	—	—	—	—	—	8
Celanese Corporation of America	—	—	1	1	2	—	3	2	—	—	—	—	9
Columbia Engineerng and Management Corporation	5	—	—	—	—	—	—	—	—	—	—	—	5
Combustion Utilities Corporation	—	6	—	—	—	—	—	—	—	—	—	—	6
Commercial Solvents Corporation	—	2	1	—	4	—	—	9	—	—	—	—	16
E. I. du Pont de Nemours & Company**	17	5	2	—	12	1	—	9	—	—	—	—	46
Hydrocarbon Synthesis Corporation	—	—	—	15	—	—	9	—	—	—	—	—	24
I. G. Farbenindustrie A.-G.	14	11	16	14	16	—	—	—	1	—	2	2	76
M. W. Kellogg Company	6	—	—	4	—	—	2	—	1	—	1	—	14
Koppers Company	5	17	6	2	—	—	—	—	—	7	—	—	37
Phillips Petroleum Company	—	—	5	—	—	—	—	—	—	—	—	—	5
The Selden Company	—	1	—	4	1	—	2	—	—	—	—	—	8
Shell Development Company***	4	—	1	—	—	—	2	—	—	—	—	—	7
Solvay Process Company****	3	5	—	—	1	—	1	—	—	11	—	—	21
Standard Oil Company (N. J.)*****	25	—	3	23	1	8	3	—	—	1	1	—	64
Standard Oil Company (Ind.)	2	—	—	4	—	—	—	—	—	—	—	—	6
Universal Oil Products Company	—	—	3	2	1	—	—	—	—	—	—	—	6
Western Gas Construction Company	—	3	—	—	—	—	—	—	—	—	—	—	7
Other Companies	20	20	21	25	6	1	4	1	2	4	—	—	122
Individuals	38	60	16	29	16	—	6	3	1	48	2	1	219
Grand Total	145	131	75	130	64	10	32	24	5	91	6	3	716

* As of January 1, 1945.
** Including patents granted to subsidiaries and absorbed companies.
*** Including patents granted to N. V. de Bataafsche Petroleum Maatschappij.
**** Including patents granted to Semet-Solvay Engineering Company, also an Allied Chemical subsidiary.
***** Including patents granted to Standard Catalytic Company, Standard-I. G Company, and Standard Oil Development Company.

United States with the advent of full-scale operations (or even before this).

Variations of the Fischer-Tropsch process can produce practically all of the "quality" petroleum products; in fact, P. C. Keith has pointed out that one barrel of synthetic crude is the equivalent of 1.4 barrels of crude petroleum in terms of recoverable products.[14]

Assuming—as seems likely upon sober analysis—that nuclear energy will not materially affect the demand for "quality" petroleum products in the predictable future, whatever it may do to markets for coal and heavy fuel oils—it seems likely that the Fischer-Tropsch process will continue of great interest to the petroleum industry and will come into wide use if and when the supply of crude petroleum in the United States fails to meet demands or becomes sufficiently high in cost to make such use definitely economic. National security is another factor to be considered.

This book, despite its detailed appendices, has by no means exhausted the literature on the Fischer-Tropsch process. Nevertheless, it has indicated that the petroleum industry and other interested industries have available a vast storehouse of information upon which to base their future research and operations. The success of these endeavours in the U.S.A. seems assured, dependent as they are upon the technical genius of a nation whose armies, in war, are better equipped than those of any other country, and whose citizens, in peace, have been provided with—have provided for themselves—the highest standard of living in the world.

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[13] Anon., *National Petroleum News* **38,** No. 24, 50 (1946).
[14] Anon., *National Petroleum News* **38,** No. 27, R-560 (1946).
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[19] Koch, F. C., *Oil and Gas Journal* **43,** No. 22, 56 (1944).
[20] Ratcliff, J. D., *Collier's,* November 24, 1945, p. 26.
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Part V

APPENDICES

Appendix I

FISCHER-TROPSCH PATENTS

PATENTS on any process are of interest for two reasons: (1) the legal protection given to the inventors, necessitating caution on the part of others lest they infringe on patent rights, and (2) the technical information, often unpublished elsewhere, that is contained therein and that is vital to further effective research.

Many key patents on the Fischer-Tropsch process have already been mentioned in the body of this book and are contained in chapter bibliographies, but no attempt has been made to include reference to all of the thousands of related patents. Even here, it is impossible to say that all pertinent patents have been included in the following list, although every effort has been made to accomplish this.

As far as they could be identified, the patents of all countries have been classified here since, even though patents have no legal significance for operations outside the country of their origin, they often contain information not otherwise obtainable. Considerable duplication has undoubtedly been occasioned by this decision, however, since identical patents are often obtained by companies operating in several countries and desiring patent protection therein.

The Fischer-Tropsch process, as this book has evidenced, is a complex synthesis which involves several distinct sub-processes. For purposes of classification, therefore, the following system has been used in an effort to render more accessible the patents on any phase:

A. Preparation of the Synthesis Gas Mixture

1. From Hydrocarbons (Methane-Steam Reaction, Partial Oxidation, Reaction with Carbon Dioxide, Etc., Including Hydrogen and/or Carbon Monoxide Enrichment Processes)
2. By the Water-Gas and Similar Processes (from Coke, Coal Etc.)
   a. Methods of Obtaining Hydrogen for Water-Gas Enrichment
3. Purification of the Synthesis Gas Mixture

B. The Catalytic Hydrogenation of Carbon Monoxide

1. For the Synthesis of Hydrocarbons
   a. Synthesis of Lubricants from Fischer-Tropsch Intermediates
   b. Further Refining, Synthesis of Chemical Derivatives, Etc.

2. Synthesis of Methanol and/or Higher Oxygenated Hydrocarbons

C. Catalysts for the Fischer-Tropsch and Related Processes

1. For the Preparation of the Synthesis Gas
   a. From Hydrocarbons
   b. By the Water-Gas and Similar Processes
2. For the Synthesis of Hydrocarbons
3. For the Synthesis of Methanol and/or Other Oxygenated Compounds

D. Apparatus for the Fischer-Tropsch and Related Processes

1. For Producing Synthesis Gas Mixtures
   a. From Hydrocarbons
   b. By the Water-Gas and Similar Processes
2. For Accomplishing Catalytic Syntheses
   a. Hydrocarbon Production
   b. Oxygenated Hydrocarbons Production

It is at once evident that patent listings under several of these classifications would be impossibly voluminous if they contained references to the pertinent art in all related fields. However, every effort has been made to include all patents specifically related to the Fischer-Tropsch process or directly pertaining thereto, with the following exceptions: (1) patents that deal only with the desulphurization of natural gas are not included, even though several such methods will undoubtedly be used for natural gas (but not for "coal" gases) instead of after-purification of the synthesis gas; (2) patents that deal with the synthesis of lubricants but do not mention Fischer-Tropsch intermediates even though directly analogous to those that do; lengthy surveys on this subject are available elsewhere; (3) patents on hydrocarbon refining and chemical synthesis that do not mention the Fischer-Tropsch process—to include these would have required a complete list of all petroleum refining patents; (4) patents that deal with water-gas synthesis apparatus (including water-gas enrichment) but are not pertinent to hydrocarbon synthesis; and (5) patents on hydrogen synthesis by electrolysis and other non-economic methods for large-scale use.

In general, patents of all countries have been cross-classified under all pertinent subjects. This classification, for the years prior to 1943, was the work of several people and may not have been done in a perfectly uniform manner, but reference to related classes will in any case provide reasonable completeness; i.e., a person interested in patents on apparatus for the synthesis of hydrocarbons should

certainly also consult Section B, 1, the section on the synthesis itself.

No attempt has been made to list unissued German patent applications, information on some of which is gradually becoming available from the Office of Technical Services, but a number of enemy-owned, unfiled or abandoned United States patent applications (APC, TC and APC, SN numbers) have been listed along with United States patents, as have as yet unissued United States patent applications (APC numbers) which are also currently being licensed by the Alien Property Custodian. It is probable that ownership of some of the latter has since been returned to their original assignees, by court action and otherwise.

No attempt can be made here to discuss the legal or other significance of these patents. Table XXIV in Chapter 20 is indicative of patent holdings but is by no means a quantitative measure of their importance, since a patent licence can be far more valuable than the possession of a dozen patents. It is unfortunate that space requirements prevent the publication here of patent abstracts instead of listings, but this can be remedied by the interested reader through reference to *Chemical Abstracts*, *British Chemical Abstracts*, the *Chemisches Zentralblatt*, and the *Official Gazette* of the United States Patent Office.

A. Preparation of the Synthesis Gas Mixture

1. From Hydrocarbons (Methane-Steam Reaction, Partial Oxidation, Reaction with Carbon Dioxide, etc., including Hydrogen and/or Carbon Monoxide Enrichment Processes)

Austrian Patents

8119/1927	121,228		

Belgian Patents

287,296	361,718	387,055	416,369

British Patents

16,373	271,483	319,957	341,393
26,666	271,491	323,864	342,817
163,703	274,610	327,025	343,172
244,730	288,662	328,048	357,956
247,176	291,244	335,524	360,081
254,713	300,328	335,632	360,148
265,989	301,969	336,635	364,106
266,410	307,529	337,410	364,419
267,535	314,870	338,905	366,107
269,247	317,731	340,059	366,360

A. Preparation of the Synthesis Gas Mixture

1. From Hydrocarbons (*continued*)

British Patents (*continued*)

366,369	390,849	480,820	554,080
370,457	391,532	493,259	554,095
373,701	454,173	513,778	573,925
376,358	458,022	517,744	574,048
379,014	458,557	525,803	575,377
381,072	458,692	528,826	575,378
386,981	466,737	547,881	

Canadian Patents

187,661	285,619	337,632	395,969
264,324	319,121	348,001	411,292

French Patents

35,613	682,550	715,792	771,792
371,192	684,579	723,817	784,742
421,838	685,854	723,966	805,699
463,114	700,570	724,825	817,767
632,660	701,003	731,652	832,038
632,861	704,601	733,248	834,686
672,935	711,813	734,032	845,361
677,826	712,092	742,842	845,492
682,549	713,487	758,878	

German Patents

229,406	552,446	585,420	699,489
296,866	554,551	594,395	701,846
306,301	558,430	601,305	703,561
403,049	567,069	602,111	712,554
507,917	570,026	606,841	728,547
514,394	578,824	646,915	730,346
525,556	581,986	652,248	730,409
529,048	583,205	673,773	739,445
534,906	584,538	682,018	741,681
538,012	585,419	685,443	745,069
546,205			

Italian Patent

295,635

A. Preparation of the Synthesis Gas Mixture
1. From Hydrocarbons (*continued*)

Japanese Patents

95,140 98,957 134,216

Polish Patents

10,425 10,914

Swiss Patent

127,030

United States Patents

Re. 18,382	1,892,973	1,957,744	2,125,743
314,342	1,896,420	1,959,151	2,135,058
1,107,581	1,899,184	1,959,189	2,135,694
1,107,582	1,901,136	1,959,924	2,135,695
1,128,804	1,903,845	1,960,886	2,164,292
1,134,416	1,904,426	1,960,912	2,164,403
1,228,818	1,904,439	1,962,418	2,170,265
1,252,033	1,904,441	1,970,695	2,173,695
1,699,177	1,904,592	1,972,259	2,173,984
1,711,036	1,904,593	1,983,992	2,182,747
1,713,325	1,905,326	1,984,380	2,185,989
1,716,813	1,911,780	2,013,066	2,198,553
1,723,772	1,913,237	2,013,699	2,199,475
1,734,559	1,915,362	2,018,118	2,220,849
1,736,065	1,915,363	2,022,778	2,234,941
1,762,100	1,919,857	2,028,326	2,243,869
1,794,004	1,920,858	2,030,283	2,252,810
1,799,452	1,921,856	2,032,566	2,253,607
1,826,974	1,923,656	2,038,566	2,256,333
1,830,010	1,929,664	2,039,459	2,258,511
1,831,943	1,930,442	2,039,603	2,266,989
1,834,115	1,930,443	2,042,285	2,268,910
1,841,201	1,931,442	2,051,363	2,270,897
1,843,063	1,934,836	2,052,149	2,313,157
1,863,681	1,938,202	2,056,911	2,322,989
1,870,144	1,948,338	2,064,867	2,324,172
1,874,801	1,951,044	2,067,729	2,337,551
1,875,253	1,951,774	2,083,795	2,346,754
1,875,923	1,953,047	2,084,511	2,349,438
1,882,977	1,955,290	2,119,565	2,355,052
1,889,530	1,957,743	2,119,566	2,360,463

A. Preparation of the Synthesis Gas Mixture

1. From Hydrocarbons (*continued*)

United States Patents (continued)

2,377,993	2,400,075	APC,TC	APC,TC
2,383,715	APC	1,122	1,153
2,389,636	303,852		

2. By the Water-Gas and Similar Processes (from Coal, Coke, etc.)

Australian Patent

113,892

Austrian Patents

71,698	124,062	149,657	156,174
121,094	146,202	155,402	157,415
122,963	146,939	155,632	157,970
122,980			

Belgian Patent

426,221

British Patents

884	214,544	250,626	282,690
2,676	219,865	251,530	288,336
5,730	219,866	255,279	288,426
5,737	224,950	255,637	288,463
8,154	231,866	260,511	288,797
10,325	234,929	261,362	289,058
13,160	235,007	268,599	289,080
14,703	235,958	269,234	294,611
15,964	236,579	269,936	295,717
19,101	238,177	270,009	296,064
24,374	238,987	270,429	299,315
124,798	239,280	272,026	299,421
164,935	241,991	272,822	299,485
165,616	242,237	274,610	301,459
189,789	243,414	276,753	307,529
196,658	247,803	279,316	310,686
197,798	249,772	282,141	312,533
212,943	250,289	282,573	317,460

A. Preparation of the Synthesis Gas Mixture

2. By the Water-Gas and Similar Processes (*continued*)

British Patents (*continued*)

318,174	349,459	457,181	523,221
323,042	351,828	458,022	531,288
329,751	353,522	459,314	531,289
330,221	353,998	465,548	532,885
330,918	373,480	466,737	534,517
336,821	382,406	470,275	542,511
336,965	382,597	473,948	554,080
337,807	389,377	476,879	554,095
341,001	391,682	487,714	554,869
341,370	391,780	493,046	559,916
342,229	396,718	499,018	561,338
342,817	406,578	502,147	570,007
344,205	416,936	504,529	573,923
345,858	439,562	508,617	573,924
347,520	450,544	516,546	575,377
347,601	452,538	517,530	575,378
348,207	456,671	521,425	577,015

Canadian Patents

206,164	281,814	322,679	423,352
230,652	284,248	355,666	423,377
245,557	289,830	361,530	426,582
274,130	295,969	361,885	

Dutch Patent

7,399

French Patents

349,426	669,788	723,109	812,376
466,309	672,164	731,052	816,165
484,973	680,849	743,915	817,210
634,711	681,147	755,142	820,590
636,750	689,854	759,246	827,488
639,683	690,126	761,506	845,209
645,780	693,105	777,546	845,252
649,296	697,489	784,742	845,316
658,586	699,128	801,309	846,588
659,426	705,144	801,380	851,502
659,427	706,505	807,793	852,015
663,134	709,219	810,012	852,016
666,357			

A. Preparation of the Synthesis Gas Mixture

2. By the Water-Gas and Similar Processes (*continued*)

German Patents

205,252
237,283
245,039
253,706
263,025
275,221
285,703
422,999
437,970
438,843
484,003
487,886
490,981
492,088
492,277
493,675
494,240
495,372
496,342
497,894
498,225
503,410
503,704
505,034
509,291
516,655
516,786
517,066
517,469
518,427
531,822
533,111
534,328
535,672
539,891
540,316
540,548
541,686
543,487
553,036
567,375
569,211
571,168
571,210
582,495
596,839
597,240
605,744
612,046
614,928
628,193
630,963
645,297
649,162
659,956
661,172
669,434
681,155
693,518
696,669
701,758
702,605
703,880
710,724
716,078
717,193
719,874
723,163
724,873
728,547
729,338
730,308
741,681

Hungarian Patent

127,066

Italian Patents

305,331
328,034
333,191
346,263

Japanese Patents

90,292
101,999
129,729
131,514
133,467

Polish Patent

10,649

Russian Patent

34,690

A. Preparation of the Synthesis Gas Mixture

2. By the Water-Gas and Similar Processes (*continued*)

Swedish Patent

41,792

Swiss Patent

162,458

United States Patents

898,803	1,712,983	1,809,421	2,062,537
981,708	1,713,189	1,842,263	2,066,670
1,061,861	1,716,667	1,848,015	2,070,099
1,154,455	1,745,454	1,857,799	2,093,005
1,159,675	1,751,117	1,860,138	2,111,579
1,214,164	1,752,035	1,872,883	2,132,533
1,251,252	1,752,036	1,873,941	2,148,298
1,268,763	1,752,037	1,894,180	2,148,299
1,379,038	1,766,763	1,920,626	2,151,121
1,405,863	1,771,067	1,921,711	2,153,820
1,409,682	1,776,876	1,923,540	2,168,933
1,447,839	1,780,759	1,923,541	2,172,740
1,505,065	1,784,765	1,947,614	2,175,613
1,587,588	1,785,519	1,949,563	2,204,001
1,592,861	1,788,170	1,962,616	2,204,003
1,605,646	1,790,824	1,963,167	2,220,357
1,631,823	1,791,411	1,966,886	2,302,157
1,682,264	1,792,632	1,977,684	2,276,343
1,701,253	1,799,359	2,010,634	2,332,781
1,709,107	1,808,214	2,035,600	2,361,292
1,709,335	1,808,672		

a. Methods of Obtaining Hydrogen for Water-Gas Enrichment

Austrian Patents

111,555 126,350

Belgian Patent

376,567

A. Preparation of the Synthesis Gas Mixture

2. By the Water-Gas and Similar Processes

a. Methods of Obtaining Hydrogen for Water-Gas Enrichment (*continued*)

British Patents

12,978	276,687	352,688	507,120
13,397	292,342	352,864	525,803
24,256	300,328	355,861	527,243
26,808	322,701	356,838	538,348
231,218	332,057	365,902	543,626
259,643	335,869	431,970	546,177
267,535	336,635	450,416	547,155
271,483	336,944	454,173	548,183
271,491	340,822	490,920	549,838
271,767	349,060	493,259	

Canadian Patent

407,876

Czechoslovakian Patents

50,853 51,421

Dutch Patent

44,648

French Patents

49,225	683,625	710,626	825,708
49,519	690,533	720,338	834,031
361,492	698,484	724,825	853,200
654,277	698,706	801,469	853,201

German Patents

516,843	675,431	719,451	737,786
617,477	706,868	725,157	

Japanese Patent

132,307

A. Preparation of the Synthesis Gas Mixture

2. By the Water-Gas and Similar Processes

a. Methods of Obtaining Hydrogen for Water-Gas Enrichment (*continued*)

Russian Patent

48,221

Swiss Patent

178,788

United States Patents

Re. 21,521	1,703,747	1,896,916	2,032,566
229,338	1,723,772	1,897,725	2,038,440
229,339	1,756,934	1,898,527	2,053,650
229,340	1,781,935	1,898,967	2,057,402
265,915	1,789,538	1,901,885	2,083,440
278,145	1,793,677	1,903,247	2,116,993
278,146	1,794,231	1,904,441	2,147,780
314,342	1,797,426	1,904,592	2,153,664
854,157	1,812,526	1,904,593	2,182,747
873,853	1,812,527	1,904,908	2,183,301
964,415	1,815,090	1,915,363	2,198,560
1,027,862	1,816,523	1,920,858	2,229,166
1,027,863	1,817,726	1,931,492	2,271,214
1,107,926	1,826,974	1,933,069	2,284,468
1,126,371	1,830,010	1,934,029	2,293,241
1,134,416	1,831,943	1,934,075	2,313,457
1,276,385	1,834,116	1,935,675	2,315,424
1,276,487	1,834,540	1,938,087	2,328,828
1,411,760	1,869,825	1,938,202	2,338,402
1,424,749	1,880,924	1,959,924	2,364,562
1,583,673	1,881,490	1,977,992	APC
1,597,277	1,889,672	1,985,441	347,565
1,673,032	1,892,559	1,988,759	APC,TC
1,689,858	1,896,240	2,000,224	1,126

3. Purification of the Synthesis Gas Mixture

Belgian Patents

444,769 447,709

A. Preparation of the Synthesis Gas Mixture

3. Purification of the Synthesis Gas Mixture (*continued*)

British Patents

130,654	340,016	421,963	528,848
254,288	341,444	434,673	533,009
276,687	351,975	452,717	545,767
282,634	358,851	457,343	547,155
287,106	369,490	461,001	550,113
287,558	370,466	469,933	553,414
289,885	370,911	478,877	561,579
298,236	370,978	481,850	561,673
305,026	371,117	490,775	561,679
305,027	384,532	491,299	563,350
315,868	391,660	497,301	567,273
330,933	400,387	507,593	572,471

Canadian Patent

266,382

Dutch Patents

22,257 23,374

French Patents

642,892	702,777	723,487	797,902
653,503	709,464	735,331	847,326
669,421	714,825	741,372	849,158
669,929	720,740	784,337	849,527
693,106	723,443	787,782	853,404

German Patents

448,156	604,294	710,027	724,911
448,298	607,819	712,026	725,055
462,837	646,172	712,450	729,889
545,368	651,462	713,582	733,677
558,558	671,189	715,479	735,662
567,843	700,598	716,351	737,031
570,449	706,846	717,940	740,406
583,387	707,914	719,874	743,995
589,073	708,031	721,024	745,242
603,526	708,933		

A. Preparation of the Synthesis Gas Mixture

3. Purification of the Synthesis Gas Mixture (*continued*)

Italian Patent

272,092

Russian Patents

52,333 55,390 57,803 59,093

United States Patents

911,494	1,852,497	2,029,100	2,310,784
1,504,624	1,854,491	2,041,840	2,315,662
1,624,625	1,854,511	2,045,747	2,315,663
1,695,130	1,891,974	2,083,894	2,318.522
1,717,761	1,895,724	2,083,895	2,355,147
1,741,834	1,897,725	2,094,844	2,357,355
1,757,826	1,900,751	2,106,446	2,357,734
1,760,522	1,900,882	2,110,240	2,365,202
1,774,366	1,900,883	2,110,241	2,368,595
1,775,366	1,911,498	2,124,260	2,368,600
1,782,590	1,916,824	2,137,602	2,369,432
1,812,526	1,925,027	2,143,393	2,379,076
1,812,527	1,947,776	2,151,721	2,384,065
1,815,846	1,950,981	2,161,663	2,388,259
1,818,615	1,962,051	2,169,282	2,398,919
1,819,055	1,976,806	2,176,441	2,403,319
1,822,293	1,983,313	2,193,278	2,405,672
1,847,795	1,990,217	2,239,000	APC
1,851,312	2,007,741	2,259,409	362,357
1,852,014	2,008,953	2,288,749	APC
1,852,160	2,011,386	2,299,149	398,345
1,852,161	2,024,393	2,301,588	

B. The Catalytic Hydrogenation of Carbon Monoxide

1. For the Synthesis of Hydrocarbons

Belgian Patents

418,230 418,492 424,929 427,333

B. The Catalytic Hydrogenation of Carbon Monoxide
1. For the Synthesis of Hydrocarbons (*continued*)

British Patents

20,488	316,216	480,442	516,352
196,023	316,945	482,783	516,403
223,543	317,460	486,926	517,002
247,178	319,340	487,250	518,372
252,786	322,284	495,575	518,605
255,818	342,817	496,159	518,614
255,828	352,864	496,292	519,613
255,829	356,838	496,880	519,722
261,267	357,206	500,264	526,465
262,494	365,544	500,950	526,814
263,503	365,902	502,542	528,617
269,251	394,506	502,771	529,390
270,705	449,274	503,247	534,357
271,767	454,948	503,622	536,767
279,347	457,934	504,910	536,843
282,573	458,035	505,121	538,225
282,690	462,242	506,064	542,836
286,255	464,308	507,366	545,695
291,867	465,668	507,567	551,312
293,185	468,434	509,325	559,044
293,572	469,618	510,350	564,730
297,179	469,959	510,513	567,609
309,002	471,482	510,514	573,982
310,999	471,595	513,674	574,048
312,916	478,318	515,037	575,377
313,467	479,931	516,329	575,378
			575,829

Canadian Patents

265,063	299,868	411,292	421,168
284,235	371,802		

Czechoslovakian Patents

33,469	51,421

B. The Catalytic Hydrogenation of Carbon Monoxide
1. For the Synthesis of Hydrocarbons (*continued*)

French Patents

48,512	726,045	815,200	834,328
48,739	742,728	815,351	834,686
48,876	784,742	815,716	836,273
49,333	788,286	820,757	836,701
51,588	802,208	823,262	836,937
355,900	802,536	823,302	839,061
613,542	804,626	824,002	840,568
631,927	805,696	824,216	841,030
635,950	809,226	824,893	841,043
643,784	812,290	825,379	842,507
647,981	812,598	830,289	843,370
660,133	812,883	830,560	843,844
680,619	814,082	830,871	843,874
707,607	814,636	832,038	853,302
719,035	814,853	832,967	870,679

German Patents

293,787	630,824	711,422	734,218
457,563	637,446	713,792	734,993
458,756	672,731	716,854	736,091
484,337	693,370	720,685	736,701
524,468	703,101	721,359	736,844
528,740	703,225	722,706	737,620
531,004	705,528	724,054	738,091
567,069	708,512	728,217	739,569
571,898	708,889	728,766	742,376
578,311	710,128	729,290	744,184
597,515	710,963	733,841	744,185

Indian Patents

22,982	22,662	25,177	25,273

Italian Patents

341,317	345,513	346,769	361,595
344,270	345,671	351,714	390,547
345,471	346,389	352,319	

Japanese Patents

130,421	130,554	133,533	

B. The Catalytic Hydrogenation of Carbon Monoxide
1. For the Synthesis of Hydrocarbons (*continued*)

Jugoslavian Patent

14,629

Norwegian Patents

56,163 57,461

Russian Patents

53,249 54,392

Swiss Patent

229,187

United States Patents

Re. 22,415	1,977,718	2,220,261	2,257,074
Re. 22,205	1,979,841	2,220,357	2,257,293
956,734	1,988,873	2,224,048	2,257,457
983,199	2,002,534	2,224,049	2,258,511
989,755	2,033,914	2,225,487	2,258,839
1,201,850	2.039,459	2,231,990	2,259,961
1,591,526	2,116,081	2,234,568	2,261,184
1,640,668	2,127,127	2,234,941	2,264,427
1,643,663	2,128,994	2,238,240	2,265,094
1,698,602	2,148,545	2,238,726	2,271,259
1,735,925	2,149,515	2,238,766	2,274,064
1,741,306	2,151,329	2,238,846	2,274,639
1,741,307	2,159,077	2,243,869	2,274,750
1,741,308	2,159,140	2,243,897	2,276,274
1,743,214	2,161,974	2,244,196	2,279,052
1,746,464	2,167,004	2,244,710	2,281,362
1,772,652	2,172,441	2,247,087	2,284,468
1,798,288	2,178,824	2,248,099	2,286,814
1,801,382	2,180,672	2,248,734	2,287,092
1,831,179	2,183,145	2,250,421	2,287,891
1,832,762	2,183,146	2,251,554	2,296,405
1,836,085	2,206,500	2,253,607	2,301,687
1,851,762	2,207,581	2,254,748	2,318,602
1,860,138	2,209,190	2,254,806	2,318,626
1.940,209	2,211,022	2,255,126	2,324,172
1,940,944	2,213,415	2,256,622	2,338,475

B. The Catalytic Hydrogenation of Carbon Monoxide

1. For the Synthesis of Hydrocarbons (*continued*)

United States Patents (*continued*)

2,338,505	2,361,997	2,398,462	APC
2,339,927	2,363,739	2,400,075	390,534
2,345,957	2,365,029	2,406,851	APC
2,347,682	2,369,106	APC	414,926
2,348,699	2,369,956	369,127	APC,TC
2,349,915	2,377,245	APC	1,222
2,351,248	2,384,874	373,942	APC,TC
2,353,600	2,393,420	APC	1,225
2,354,540	2,393,909	382,639	
2,360,787			

a. Synthesis of Lubricants from Fischer-Tropsch Intermediates

British Patents

322,284	473,935	490,930	495,477
449,274	483,316	491,778	503,206
453,973	485,165	493,715	504,350
470,534	485,478	494,657	575,378

French Patents

792,021	809,226	827,761	840,890
799,058	825,839		

German Patent

726,885

United States Patents

1,309,432	2,172,441	APC	APC
1,798,288	2,199,200	210,424	382,394
2,159,148	2,238,846		

b. Further Refining, Synthesis of Chemical Derivatives, etc.

Belgian Patents

443,918	444,625

B. The Catalytic Hydrogenation of Carbon Monoxide

1. For the Synthesis of Hydrocarbons

b. Further Refining, Synthesis of Chemical Derivatives, etc. (*continued*)

British Patents

354,215	487,317	491,221	507,521
464,393	489,443	492,595	552,731
482,277	490,785	506,104	574,973

French Patents

818,056	819,659	823,262	837,524

German Patents

709,843	719,449	725,485	738,709
712,293	721,945	726,197	739,570
713,627	722,591	733,749	740,294
714,489	725,000	736,094	742,054

Italian Patent

352,074

Norwegian Patent

65,700

United States Patents

1,704,732	2,257,074	APC	APC
2,045,795	2,268,939	129,813	362,684
2,073,054	2,281,362	APC	APC
2,159,148	2,322,622	264,995	373,703
2,224,003	2,391,236	APC	APC
2,242,321	2,398,489	280,054	383,242
2,243,760	APC	APC	APC,TC
2,245,157	60,192	280,055	1,156

B. The Catalytic Hydrogenation of Carbon Monoxide

2. Synthesis of Methanol and/or Higher Oxygenated Hydrocarbons

Belgian Patent

445,858

British Patents

9,762	247,178	266,405	306,512
227,149	247,932	266,410	313,467
228,959	252,361	269,251	317,460
229,714	252,362	271,538	317,808
229,715	252,786	278,777	335,962
237,030	262,494	282,573	337,410
238,319	262,832	300,294	338,854
247,176	263,503		

Canadian Patents

251,483	251,485	271,569	286,288
251,484	251,486	284,235	359,414

French Patents

635,950	733,248	814,434	835,899
643,784	799,270	817,767	847,617
705,590			

German Patents

293,787	508,953	568,627	628,427
462,837	544,665	600,677	628,557
484,166	548,434	608,361	646,928
489,280	559,892	614,928	671,606
490,248	565,309	614,975	708,512
492,245	565,880	625,757	721,359

Russian Patent

47,687

B. The Catalytic Hydrogenation of Carbon Monoxide

2. Synthesis of Methanol and/or Higher Oxygenated Hydrocarbons (*continued*)

United States Patents

Re. 19,243	1,741,307	1,859,244	2,014,883
1,201,850	1,741,308	1,864,531	2,059,495
1,235,426	1,743,214	1,868,096	2,061,470
1,431,047	1,744,180	1,875,273	2,111,469
1,460,244	1,746,781	1,875,714	2,115,553
1,558,559	1,746,782	1,889,251	2,159,077
1,562,480	1,746,783	1,896,224	2,205,542
1,569,775	1,754,371	1,917,323	2,242,463
1,679,256	1,757,441	1,921,776	2,266,161
1,684,640	1,770,165	1,942,530	2,279,153
1,685,759	1,791,568	1,946,918	2,281,228
1,704,214	1,797,569	1,959,219	2,327,066
1,704,732	1,815,677	1,963,119	2,346,701
1,704,751	1,818,165	1,977,718	2,349,915
1,735,925	1,829,046	1,984,884	APC
1,738,971	1,831,179	1,996,101	377,406
1,738,989	1,836,085	2,000,096	APC,TC
1,740,140	1,841,910	2,014,757	1,196
1,741,306	1,844,129		

C. Catalysts for the Fischer-Tropsch and Related Processes

1. For Preparation of the Synthesis Gas

a. From Hydrocarbons

British Patents

26,666	314,870	366,107	376,358
266,410	314,944	366,360	379,014
267,535	323,855	370,457	421,963
271,523	360,081	373,701	485,178
301,969	364,419		

Canadian Patents

310,207	337,632	348,001

Danish Patent

53,291

C. Catalysts for the Fischer-Tropsch and Related Processes

1. For Preparation of the Synthesis Gas

a. From Hydrocarbons (*continued*)

Dutch Patent

23,021

French Patents

463,114	704,601	715,792	733,248
632,861	710,626	724,825	734,032
677,826	711,813	729,119	771,792
701,003	713,487	731,652	845,492

German Patents

306,301	546,205	570,026	601,305
525,556	552,446	585,419	602,111
534,906	554,551	594,395	606,841
538,012	567,069		

Japanese Patent

134,216

Swiss Patent

127,030

United States Patents

Re. 21,521	1,920,858	2,030,283	2,125,743
1,128,804	1,931,492	2,032,566	2,135,058
1,711,036	1,934,836	2,039,603	2,137,101
1,713,325	1,938,202	2,042,285	2,164,292
1,799,452	1,943,821	2,056,911	2,173,984
1,826,974	1,948,338	2,057,402	2,209,492
1,830,010	1,957,743	2,064,867	2,220,849
1,834,115	1,959,189	2,067,729	2,229,199
1,863,681	1,968,063	2,083,795	2,270,897
1,874,801	1,970,695	2,112,387	2,284,468
1,904,440	1,984,380	2,119,565	APC,TC
1,904,441	1,998,401	2,119,566	1,153
1,915,362	2,013,066		

C. Catalysts for the Fischer-Tropsch and Related Processes

1. For Preparation of the Synthesis Gas

b. By the Water-Gas and Similar Processes

British Patent

424,478

Dutch Patent

44,648

French Patent

777,546

German Patents

237,283 630,963

Japanese Patents

91,310 132,307 132,592 133,467
129,729 132,543 133,237

Swiss Patent

178,788

United States Patents

1,834,116 2,106,597 2,197,707

2. For the Synthesis of Hydrocarbons

Australian Patents

4473/1931 106,295 106,931 111,151
103,630

Austrian Patent

142,219

Belgian Patents

445,023 446,167

C. Catalysts for the Fischer-Tropsch and Related Processes

2. For the Synthesis of Hydrocarbons (*continued*)

British Patents

20,488	319,340	496,292	516,329
223,543	322,284	496,880	517,002
254,713	352,864	498,007	518,334
255,818	365,544	500,182	526,465
255,828	394,506	500,264	526,814
255,829	453,973	500,950	528,617
263,503	457,934	502,542	528,826
269,251	465,157	502,771	529,390
270,705	465,668	503,622	530,036
271,452	468,434	504,700	533,459
282,573	469,959	504,910	534,357
282,690	471,595	505,121	534,367
286,255	473,932	506,064	536,767
291,867	474,448	507,366	536,843
293,185	478,318	507,419	536,912
293,572	480,442	509,325	538,225
297,179	484,337	510,350	542,836
312,717	484,962	510,514	545,695
312,916	490,090	515,037	564,730
313,467	491,778	516,160	575,829
316,945			

Canadian Patents

284,235	371,802	411,292	425,132

Czechoslovakian Patent

33,469

Dutch Patent

50,858

French Patents

48,512	49,333	355,900	631,927
48,739	49,424	613,542	635,950

C. Catalysts for the Fischer-Tropsch and Related Processes

2. For the Synthesis of Hydrocarbons (*continued*)

French Patents (*continued*)

643,784	814,636	826,820	842,278
660,133	815,200	830,289	842,507
707,607	815,351	830,560	843,305
714,825	815,716	834,328	843,370
726,045	819,701	836,273	843,844
784,742	824,216	840,568	845,301
812,290	824,893	841,030	870,679

German Patents

484,337	685,371	721,359	736,701
524,468	700,434	722,553	736,922
531,004	705,528	722,706	736,977
567,069	707,414	728,217	738,091
571,898	708,512	728,766	738,368
597,515	710,128	729,059	742,376
630,824	710,963	729,060	744,048
637,446	720,107	729,290	745,444

Indian Patents

22,776	25,177

Italian Patents

341,317	345,513	349,478	352,319
344,270	345,671	351,714	361,595
345,471			

Japanese Patents

130,554	133,533

Norwegian Patents

56,163	57,461

Russian Patents

53,249	54,392

C. Catalysts for the Fischer-Tropsch and Related Processes

2. For the Synthesis of Hydrocarbons (*continued*)

United States Patents

Re. 22,415	2,127,127	2,244,710	2,365,094
983,199	2,132,613	2,246,087	2,367,239
989,755	2,136,509	2,250,421	2,369,106
1,201,850	2,151,329	2,251,554	2,369,548
1,563,587	2,156,422	2,254,748	2,369,956
1,628,190	2,159,077	2,254,806	2,398,462
1,640,668	2,167,004	2,257,293	2,399,984
1,643,663	2,178,824	2,257,457	2,406,864
1,698,602	2,180,672	2,259,961	2,407,814
1,741,306	2,183,145	2,261,184	2,407,818
1,741,307	2,183,146	2,264,427	APC
1,741,308	2,206,500	2,267,737	230,512
1,743,214	2,207,581	2,271,259	APC
1,746,464	2,211,022	2,274,639	265,605
1,798,288	2,215,885	2,276,921	APC
1,801,382	2,219,042	2,278,644	357,989
1,831,179	2,220,261	2,287,891	APC
1,834,621	2,223,777	2,289,731	369,127
1,851,762	2,224,048	2,292,570	APC
1,862,949	2,224,049	2,296,405	414,926
1,868,044	2,231,990	2,301,687	APC,SN
1,871,004	2,234,246	2,309,034	240,150
1,904,218	2,234,568	2,319,453	APC,TC
1,915,473	2,238,726	2,326,275	1,136
1,925,389	2,239,000	2,338,805	APC,TC
1,940,944	2,243,897	2,339,927	1,188
1,977,718	2,244,196	2,354,540	APC,TC
1,997,135	2,244,573	2,361,997	1,190

3. For the Synthesis of Methanol and/or Other Oxygenated Compounds

British Patents

227,147	262,832	282,573	317,808
229,714	263,503	300,294	335,962
229,715	271,523	301,806	337,410
237,030	271,538	313,061	338,854
238,319	271,840	313,093	345,645
252,361	278,777	313,467	454,428
262,494	280,522	316,113	

C. Catalysts for the Fischer-Tropsch and Related Processes

3. For the Synthesis of Methanol and/or Other Oxygenated Compounds (*continued*)

Canadian Patents

251,483	271,569	274,915	284,235
251,484	274,911	276,300	315,876
251,486	274,912	280,008	359,414
267,008			

French Patents

631,927	643,784	799,270	822,818
635,950	705,590	818,078	835,899
642,318			

German Patents

489,280	565,309	614,975	636,682
490,248	565,880	625,757	646,928
544,665	600,677	628,427	708,512
548,434	608,361	628,557	

Italian Patent

352,746

Japanese Patent

91,310

Russian Patent

47,687

United States Patents

1,201,850	1,625,924	1,681,750	1,738,971
1,460,244	1,625,925	1,681,751	1,738,989
1,558,559	1,625,926	1,681,752	1,740,140
1,562,480	1,625,927	1,681,753	1,741,306
1,569,775	1,625,928	1,685,759	1,741,307
1,608,643	1,625,929	1,695,447	1,741,308
1,609,593	1,668,838	1,707,331	1,743,214

C. Catalysts for the Fischer-Tropsch and Related Processes

3. For the Synthesis of Methanol and or Other Oxygenated Compounds (*continued*)

United States Patents (continued

1,746,781	1,831,179	1,917,323	2,000,096
1,746,782	1,841,910	1,921,776	2,003,477
1,746,783	1,844,129	1,927,728	2,014,757
1,770,165	1,844,857	1,939,708	2,014,883
1,772,652	1,859,244	1,942,530	2,061,470
1,774,432	1,864,531	1,946,918	2,066,153
1,791,568	1,868,096	1,959,219	2,111,469
1,793,350	1,875,273	1,963,119	2,159,077
1,815,677	1,889,251	1,977,718	2,193,464
1,818,165	1,900,829	1,984,884	2,266,161
1,824,896	1,908,484	1,996,101	2,279,153
1,829,046	1,908,696	1,999,388	

D. Apparatus for the Fischer-Tropsch and Related Processes

1. For Producing Synthesis Gas Mixtures

a. From Hydrocarbons

Belgian Patent

287,296

British Patents

16,373	301,969	366,360	458,557
26,666	327,025	379,014	458,692
271,483	341,393	390,849	469,959
298,108	343,172	391,532	517,744
298,236	360,148	458,022	528,826
300,328			

French Patents

371,192	677,826	805,699	845,361
421,838	782,000		

German Patents

497,827	529,045	676,919	699,489
507,917	652,248	682,018	703,561
514,394	672,731	685,443	735,219

D. Apparatus for the Fischer-Tropsch and Related Processes

1. For Producing Synthesis Gas Mixtures

a. From Hydrocarbons (*continued*)

Italian Patent

295,606

Polish Patent

10,425

United States Patents

Re. 18,382	1,951,044	2,052,149	2,256,333
Re. 21,521	1,951,774	2,164,403	2,258,511
1,265,043	1,959,151	2,170,265	2,266,989
1,736,065	1,960,886	2,173,984	2,268,910
1,762,100	1,960,912	2,178,833	2,270,897
1,841,201	1,962,418	2,185,989	2,337,551
1,843,063	1,977,992	2,198,553	2,338,506
1,892,559	1,984,380	2,220,849	2,355,052
1,894,140	1,988,759	2,230,467	2,355,753
1,903,845	2,018,118	2,232,121	2,356,084
1,913,237	2,022,778	2,243,869	2,367,928
1,923,656	2,028,326	2,252,810	2,377,993
1,934,836	2,039,603		

b. By the Water-Gas and Similar Processes

Australian Patent

111,058

Austrian Patents

122,980	145,201	146,202	149,657
124,062			

Belgian Patent

418,230

D. Apparatus for the Fischer-Tropsch and Related Processes

1. For Producing Synthesis Gas Mixtures

b. By the Water-Gas and Similar Processes (*continued*)

British Patents

304	240,440	288,797	336,965
884	240,468	289,058	337,807
1,835	241,991	292,235	338,877
2,676	242,226	292,408	339,743
5,730	242,237	292,410	340,276
5,737	246,970	293,284	341,370
5,742	247,803	294,611	342,581
6,849	249,772	295,717	342,958
8,154	250,289	295,900	344,205
13,104	250,626	296,064	345,411
15,677	251,530	296,161	345,858
15,964	253,088	296,243	346,711
17,087	254,046	297,568	347,375
17,986	254,113	299,315	348,207
19,101	255,279	299,421	349,459
24,374	255,447	299,485	351,828
112,942	255,637	300,328	352,411
164,935	260,501	302,852	353,522
165,616	260,511	304,139	357,001
196,658	261,362	306,143	359,100
213,476	263,932	306,537	363,715
213,818	266,680	308,972	363,931
214,544	266,681	310,508	364,926
216,456	269,221	310,686	366,066
217,998	269,234	311,279	366,414
219,805	270,429	317,815	366,782
219,865	271,173	318,174	368,529
219,866	271,765	320,853	369,054
223,543	272,822	323,042	370,815
224,950	275,490	324,867	370,816
226,096	275,978	325,437	371,841
229,399	276,065	326,293	373,480
230,217	276,630	326,998	373,486
231,866	276,753	327,442	381,046
234,929	278,486	328,642	386,195
235,007	279,316	328,643	387,192
235,087	281,727	329,751	389,377
235,891	282,141	330,221	391,603
235,958	283,238	330,509	391,682
236,579	285,996	331,468	395,473
238,174	286,835	333,472	395,991
238,175	287,870	333,842	396,718
238,177	288,336	335,203	399,119
238,987	288,426	336,821	400,857
239,280	288,463	336,902	403,595

D. Apparatus for the Fischer-Tropsch and Related Processes

1. For Producing Synthesis Gas Mixtures

b. By the Water-Gas and Similar Processes (*continued*)

British Patents (continued)

411,757 456,671 487,714 517,530
416,936 457,181 495,063 527,243
424,168 458,022 499,646 527,445
439,562 459,314 506,217 530,705
439,626 465,548 508,617 553,621
445,638 470,275 512,920 559,916
445,639 473,948 516,546 561,124

Canadian Patents

210,552 361,530 384,470 423,352
284,248 361,885 422,221 423,377
305,227

Danish Patent

37,567

Dutch Patent

7,399

French Patents

37,192 672,164 729,063 803,253
48,672 672,775 731,052 809,987
361,492 675,209 732,571 819,591
466,309 675,253 734,253 819,592
637,207 682,313 735,006 825,708
638,926 684,855 736,621 834,716
645,057 693,289 736,943 835,474
647,499 693,514 742,514 845,252
651,638 708,527 746,687 845,316
654,277 714,880 755,677 852,016
662,062 716,280 758,878 853,153
663,134 719,662 781,845 853,154
666,357 720,842 785,471 853,200
667,232 723,457 797,065 853,201
669,136 724,749 801,309

D. Apparatus for the Fischer-Tropsch and Related Processes

1. For Producing Synthesis Gas Mixtures

b. By the Water-Gas and Similar Processes (*continued*)

German Patents

205,252	509,291	583,415	675,399
232,218	510,328	585,531	675,942
237,026	511,563	586,672	677,351
253,706	516,655	589,129	679,961
260,592	516,786	589,728	682,034
263,025	517,066	594,095	682,600
269,349	517,469	594,639	695,515
286,600	518,427	596,839	703,747
287,252	519,913	597,240	703,880
422,999	520,739	598,496	705,781
447,756	520,849	599,292	706,304
467,561	524,504	599,855	709,634
469,086	528,880	600,302	710,724
470,328	528,892	600,825	711,522
470,653	531,208	602,082	711,719
471,328	534,328	608,313	713,209
471,329	534,660	609,995	713,823
479,028	535,672	611,014	713,913
481,751	539,891	617,769	714,072
486,557	541,686	627,213	714,748
488,252	545,972	629,445	714,961
490,981	549,453	634,074	715,531
490,982	553,036	638,640	718,340
492,085	553,232	646,853	723,163
492,277	556,604	649,162	724,874
494,240	558,140	658,654	728,975
495,371	564,607	659,956	730,308
495,225	564,870	661,172	732,627
499,305	564,988	661,182	735,329
500,594	571,168	663,025	737,154
503,704	571,210	663,335	737,155
505,034	571,492	670,139	739,738
506,565	579,552	672,543	742,272
508,588	581,986	673,073	744,841

Italian Patents

305,331	328,034

D. Apparatus for the Fischer-Tropsch and Related Processes

1. For Producing Synthesis Gas Mixtures

b. By the Water-Gas and Similar Processes (*continued*)

Japanese Patents

30,379 96,243 98,957 131,514
90,292

Russian Patents

28,609 52,521 55,178 55,584
34,690 54,511

Swedish Patent

41,792

Swiss Patent

72,358

United States Patents

960,839 1,491,036 1,713,189 1,785,519
978,268 1,497,010 1,716,667 1,790,823
991,728 1,497,098 1,718,830 1,790,824
1,018,942 1,497,246 1,736,586 1,791,411
1,027,862 1,505,065 1,743,724 1,792,178
1,027,863 1,516,217 1,743,725 1,792,632
1,065,254 1,516,218 1,748,316 1,794,906
1,072,370 1,554,073 1,751,497 1,808,214
1,100,941 1,578,306 1,752,035 1,808,672
1,115,065 1,592,464 1,752,036 1,809,333
1,119,472 1,605,081 1,752,037 1,809,421
1,134,754 1,605,646 1,752,278 1,813,970
1,152,869 1,620,864 1,753,274 1,815,090
1,268,763 1,670,611 1,753,847 1,824,764
1,276,487 1,682,264 1,756,934 1,831,066
1,306,831 1,683,155 1,764,992 1,831,788
1,400,885 1,699,231 1,767,579 1,845,745
1,405,863 1,701,253 1,771,067 1,848,015
1,409,682 1,703,747 1,772,789 1,855,309
1,442,993 1,708,375 1,776,876 1,857,799
1,447,839 1,709,107 1,778,706 1,864,009
1,459,058 1,709,335 1,780,759 1,872,883
1,485,845 1,712,983 1,784,765 1,873,941

D. Apparatus for the Fischer-Tropsch and Related Processes

1. For Producing Synthesis Gas Mixtures

b. By the Water-Gas and Similar Processes (*continued*)

United States Patents (*continued*)

1,880,162	1,961,245	2,137,723	2,252,800
1,885,549	1,962,616	2,143,017	2,252,801
1,892,456	1,963,167	2,151,121	2,268,603
1,900,958	1,964,073	2,153,057	2,274,006
1,900,959	1,966,886	2,163,148	2,281,290
1,900,961	1,967,582	2,172,740	2,302,156
1,913,646	1,977,684	2,175,613	2,302,157
1,921,711	1,984,045	2,179,560	2,302,396
1,923,540	2,010,634	2,198,560	2,306,978
1,923,541	2,029,864	2,203,137	2,332,781
1,927,529	2,035,600	2,204,001	2,360,574
1,928,086	2,039,175	2,204,003	APC
1,939,470	2,066,670	2,216,116	264,995
1,941,455	2,072,357	2,220,357	APC
1,948,094	2,074,472	2,232,121	385,193
1,949,563	2,093,005	2,242,306	APC,TC
1,951,990	2,132,533	2,248,483	1,126
1,953,061			

2. For Accomplishing Catalytic Syntheses

a. Hydrocarbon Production

Australian Patent

111,151

British Patents

252,786	458,035	496,159	528,617
266,405	460,017	496,718	536,169
279,347	464,242	502,542	551,312
310,999	464,308	516,352	559,044
313,467	479,931	516,403	567,609
454,428	495,575		

French Patents

707,607	812,598	815,716	825,379
802,208	814,853	822,636	836,273
805,696			

D. Apparatus for the Fischer-Tropsch and Related Processes

2. For Accomplishing Catalytic Syntheses

a. Hydrocarbon Production (*continued*)

German Patents

458,756	703,101	720,685	734,218
528,740	703,225	721,359	741,826
583,851	708,889	725,488	744,185
681,979	719,652		

Indian Patent

24,210

Italian Patents

351,470 345,471

United States Patents

1,823,468	2,167,004	2,256,622	2,363,874
1,845,050	2,172,441	2,257,074	2,384,874
1,869,736	2,178,824	2,258,511	2,393,420
1,995,647	2,220,357	2,258,839	APC,TC
2,014,757	2,224,048	2,266,161	1,134
2,033,914	2,224,049	2,279,052	APC,TC
2,039,459	2,238,240	2,286,814	1,142
2,128,994	2,238,766	2,353,600	APC,TC
2,148,545	2,243,869	2,357,894	1,158
2,156,422	2,248,734	2,360,787	

b. Oxygenated Hydrocarbons Production

British Patents

252,362 252,713 454,428 847,617

German Patents

559,892 568,627

United States Patents

1,870,665 2,242,463 APC 365,412

Appendix II

GOVERNMENT-RELEASED FISCHER-TROPSCH REPORTS

Introduction

The years which have followed the surrender of Germany have been marked by the emergence of a veritable flood of reports on all phases of German technology and, to the lesser extent of its scientific progress, on Japanese science and industry. As regards the information on German developments, tons of technical reports, documents, and records were seized by Allied scientific groups which followed closely behind the conquering armies even before the surrender in May, 1945. Since that time, these groups, supplemented by more recent missions, have collected additional tons of scientific and technological data (as if technical information may properly be judged by its weight) and have added information thereto through interrogation of high-ranking German scientists and through the preparation of analytical summary reports.

At no time in history has any country's technology been laid so bare to the discerning eye of the leading scientists of another nation. Moreover, this fact assumes even greater significance when it is considered that Germany is the country involved—a nation long noted for its scientific prowess.

Despite the fact that literally thousands of reports on German developments were prepared by Allied teams in 1945—original reports and summaries and translations of German material—it was not until the latter part of that year that more than a few managed to emerge from behind the veiling curtain of censorship. Utter confusion existed; a few groups in certain industries were able to make some progress in the release of de-classified reports pertinent to their fields, but even here, coverage was spotty and distribution uneven.

The task of co-ordinating the release in the U.S.A. of this vast wealth of technical data finally was placed in the hands of the Office of the Publication Board, a group established for this purpose in the United States Department of Commerce. At first, this group attempted to release the de-classified reports in mimeographed form, at very nominal prices, but it was soon forced to abandon this practice since Government policy forbade the establishment of a revolving expense fund (i.e., the receipts for the sales went into the

Government's general funds, although the cost of reproduction came from OPB's very limited allotments). Consequently, the Publication Board established a policy of depositing the original of each de-classified report with a Government agency to whose fields of study the data pertained, and then serving as a clearing house for orders for the regrettably-more-expensive microfilmed or photostated copies of these reports.

To bring each week's releases to the attention of American industry, the Office of the Publication Board (which has since been changed to and made a part of an expanded Office of Technical Services) began, in January, 1946, the issuance of a *Bibliography of Scientific and Industrial Reports*, available for a nominal fee from the Superintendent of Documents. This weekly bibliography includes brief abstracts of all reports de-classified during the week (including many reports on American wartime developments), arranged roughly under a number of industrial and scientific classifications. A much more detailed subject and report number index to these reports is maintained by the Office of Technical Services' Bibliographic and Reference Division, and periodical indexes are being gradually released to make more intelligible the thousands of pages of abstracts published in 1946 alone.

In addition to these services, the Bureau of Mines of the United States Department of Commerce has assumed the responsibility originally held by the Technical Oil Mission (of the Petroleum Administration for War) and other petroleum-industry-sponsored groups (including the Technical Advisory Committee of the Petroleum Industry War Council) and is indexing the vast collection of microfilmed data assembled by the Technical Oil Mission. in addition, the Bureau of Mines is republishing as parts of its Information Circular series such PB (Publication Board) released reports (and others) that it feels should receive wide distribution, and it is also maintaining reference rooms in Washington, where much of these data may be consulted.

The reports of Allied investigations in Germany which are most readily available in Britain are those issued by British Intelligence Objectives Sub-Committee (BIOS), Combined Intelligence Objectives Sub-Committee (CIOS), and Field Information Agency, Technical (FIAT); many of these are duplicates of those being issued in the United States, yet many more are either original or are as yet unreleased in the U.S.A. To add to the confusion, few issuing agencies are crediting authorship of the reports to the original groups—individual's names are usually carried through (with occasional inversions in order), as are report titles, but original group

names and report numbers are often lost in the melee. Thus it is all too easy for the unwary but avid searcher for information to purchase (at considerable expense) duplicates of the same reports.

Fischer-Tropsch Reports

This lengthy but all-too-incomplete description of the situation in regard to Government-issued reports on German technology is of vital significance to the understanding of (and tolerance for) the following list and subject indexes to identifiable reports on aspects of the Fischer-Tropsch process. No claim is made that this list is exhaustively complete; the lapse in time between final preparation and publication would render any such statement false were it even possible to claim it.

Instead, this list is only as complete as could be determined from a subject-report number list received on November 20, 1946, through the courtesy of the Office of Technical Services, several documents and Information Circulars received on November 7, 1946, from the Foreign Synthetic Liquid Fuels Division of the Bureau of Mines; a page-by-page search through the late-1946 issues of the *Bibliography of Scientific and Industrial Reports*; and a search through a number of abstract sources which are privately available to the authors. A few more recent BIOS and CIOS reports have since been added.

After careful consideration of their vast worth, it was regretfully decided not to include references to the thousands of pertinent items available in microfilm form in the 223 reels of Technical Oil Mission microfilms. Voluminous indexes to these reels are available from the Foreign Synthetic Liquid Fuels Division of the Bureau of Mines, and copies of all or portions of the microfilm reels may be purchased from the Photoduplication Service of the Library of Congress. Large segments of these reels have appeared and are appearing as Publication Board reports, and it was felt that any attempt to interpret or abridge the Bureau of Mines' indexes would be too large a task (in time consumed and space required) for the inclusion of the data in this appendix.

For this reason, the following list is chiefly an index to Fischer-Tropsch process reports issued in 1946 by the Office of Technical Services, with reference to such additional reports, issued by other groups, as could not be identified (at least at the time) as possessing "PB" numbers. To avoid confusion and duplication, these reports are listed in alphabetical order according to the last names of the senior authors; where identifiable, report numbers of other groups are listed for each report in addition to the PB (Publication Board) number. Where possible, reference is made to the pages in the

Bibliography of Scientific and Industrial Reports on which abstracts of the reports appear.

As may be noted, each listing is given a reference number—(1), (2), (55), etc.—and these numbers are then used in the subjects classifications which follow to call attention to those reports which relate to or contain material relating to each specific subject.

At the end of certain of these subject classifications, a number of PB reports are listed (by PB number) which pertain to these subjects but not directly to the Fischer-Tropsch aspects thereof. These reports may be evaluated, if desired, by direct reference to the *Bibliography of Scientific and Industrial Reports*; their identity was provided to the authors by the Office of Technical Services.

Subject classifications (but not the system) are in general those of the Office of Technical Service, with such changes as seemed desirable from data at hand. A number of reports not listed by the OTS but included in the *Bibliography of Scientific and Industrial Reports* were classified from their abstracts. Still others, identified in various ways, were classified directly.

Following the subject classifications appears a list of definitions of the abbreviations used for report-issuing agencies and a report number index to references in the bibliography. This latter list may be used as a guide to check the bibliography for data on a report number identified elsewhere; it is relatively completed as regards PB numbers but not as regards other report-issuing groups, for aforementioned reasons.

The unravelling of the important details of German scientific and industrial activities is a process which is likely to continue for months and years. In regard to the Fischer-Tropsch process alone, as this book has indicated, much of value is evolving. This includes information which has advanced and will advance American technology by several years. Operations in the United States will certainly not be carbon copies of any or several German developments, but they will benefit immeasurably from the knowledge gained from them and the time saved in not having to perform years of painstaking experiments. It is the purpose of this appendix, insofar as is possible, to aid in the task of making this information more generally available to all who desire it.

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ABBREVIATIONS USED

BIOS, British Intelligence Objectives Sub-committee.

Bureau of Mines I.C., U.S. Department of the Interior, Bureau of Mines Information Circular.

CIOS, Combined Intelligence Objectives Sub-committee.

FIAT, Field Information Agency, Technical (Office of (U.S.) Military Government for Germany).

NTME, See USNTME.

TAC, Technical Advisory Committee (Sub-committee of the Technical Committee Petroleum Industry War Council).

TOM, U.S. Government Technical Oil Mission.

USNTME, United States Naval Technical Mission in Europe.

B.S.I.R., Bibliography of Scientific and Industrial Reports. Prepared by the Office of Technical Services, U.S. Department of Commerce.

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PB Number	*List Number*	*PB Number*	*List Number*	*PB Number*	*List Number*
6	(32)	975	(70)	4,306	(94)
9	(1)	977	(77)	4,326	(96)
10	(75)	1,018	(138)	4,328	(78)
13	(61)	1,058	(52)	4,329	(95)
17	(118)	1,062	(51)	4,486	(90)
38	(81)	1,108	(47)	5,097	(127)
100	(32)	1,110	(127)	6,299	(5)
170	(39)	1,253	(85)	6,647	(138)
163	(34)	1,270	(62)	6,650	(82)
187	(41)	1,279	(132)	6,684	(123)
225	(28)	1,291	(52)	7,917	(154)
283	(24)	1,315	(100)	7,743	(55)
284	(63)	1,366	(53)	7,745	(86)
288	(67)	1,367	(86)	9,631	(130)
289	(49)	1,393	(76)	11,194	(120)
294	(84)	1,646	(129A)	12,613	(48)
365	(20)	1,657	(150)	17,116	(6)
366	(137)	1,667	(139)	17,119	(7)
367	(25)	1,675	(33)	17,120	(8)
373	(129)	1,722	(78)	17,121	(9)
390	(72)	1,743	(40)	17,245	(10)
403	(35)	1,752	(106)	17,246	(11)
412	(25)	1,767	(74)	17,249	(12)
413	(68)	1,779	(71)	17,595	(13)
414	(106)	1,854	(45)	18,302	(99)
415	(69)	1,891	(59)	18,582	(156)
416	(44)	2,047	(155)	22,491	(116)
417	(112)	2,050	(108)	22,841	(121)
474	(73)	2,051	(26)	23,020	(43)
494	(115)	2,065	(2)	23,076	(97)
500	(108)	2,233	(79)	23,370	(14)
608	(133)	2,421	(134)	23,371	(15)
758	(102A)	2,422	(135)	23,372	(16)
768	(29)	2,423	(136)	23,377	(17)
833	(117)	2,530	(138)	23,384	(18)
853	(57)	2,534	(126)	23,750	(82A)
859	(103)	2,535	(21)	23,753	(139)
861	(23)	2,899	(3)	23,808	(31)
867	(58)	3,834	(113)	25,587	(104)
869	(37)	3,841	(114)	25,677	(111)
870	(56)	3,867	(91)	26,981	(140)
890	(49)	3,868	(92)	26,982	(141)
912	(151)	4,091	(4)	26,983	(142)
953	(126)	4,115	(36)	26,984	(143)
954	(109)	4,291	(110)	26,985	(144)

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Publication Board Reports (*continued*)

PB Number	*List Number*	*PB Number*	*List Number*	*PB Number*	*List Number*
26,986	(145)	32,578	(80)	40,518	(148)
27,316	(154)	32,714	(59)	40,519	(149)
27,692	(19)	37,163	(153)	40,925	(98)
28,554	(87)	37,231	(124)	41,229	(46)
28,746	(30)	40,038	(131)	44,664	(22)
28,883	(157)	40,516	(146)	44,962	(50)
31,278	(27)	40,517	(147)	47,864	(125)

BIOS Reports

BIOS Number	*List Number*	*BIOS Number*	*List Number*	*BIOS Number*	*List Number*
Misc.* 11	(92)	82	(154)	478	(27)
Misc. 12	(91)	86	(101)	511	(157)
Misc. 25	(134)	118	(45)	521	(80)
Misc. 26	(135)	131	(102)	591	(46)
Misc. 60	(163)	199	(128)	805	(165)
Misc. 71	(33)	275	(31)	1094	(161)
Misc. 72	(150)	326	(89)	1,142	(162)
		333	(104)	1,611	(166)
		440	(87)	1,722	(159)
		447	(66)		

* Misc. = Miscellaneous Report

Bureau of Mines Information Circulars

IC Number	*List Number*	*IC Number*	*List Number*	*IC Number*	*List Number*
7,366	(60)	7,369	(79)	7,375	(82A)
7,368	(55)	7,370	(82)	7,376	(54)

CIOS Reports

CIOS Number	*List Number*	*CIOS Number*	*List Number*
ER* 12	(32)	VI-22	
ER 19	(75)	X-18 **	(129)
ER 36	(118)	XV-5	
ER 89	(81)	XVIII-5	(20)
II-11	(39)	XXII-19	(41)

* ER = Evaluation Report

** = One volume

REPORT NUMBER INDEX TO REFERENCES IN GOVERNMENT REPORT BIBLIOGRAPHY (*continued*)

CIOS Reports (*continued*)

XXIV-9	(24)	XXX-13	(77)
XXV-1	(63)	XXX-103	(82A)
XXV-6	(25)	XXX-105	(47)
XXV-25	(67)	XXXI-23	(42)
XXV-27	(49)	XXXI-31	(96)
XXVI-2	(123)	XXXI-58	(43)
XXVI-50	(28)	XXXI-79	(139)
XXVII-18	(72)	XXXII-68	(138)
XXVII-54	(68)	XXXII-90	(79)
XXVII-60	(106)	XXXII-91	(78)
XXVII-68	(84)	XXXII-92	(51)
XXVII-69	(69)	XXXII-96	(53)
XXVII-70	(70)	XXXII-107	(64)
XXVII-82	(73)		(65)
XXVII-93	(44)		(82)
XXVIII-35	(110)		(83)
XXVIII-36	(112)		(88)
XXVIII-40	(108)		(105)
XXX-5	(126)		(152)
XXX-6	(127)	XXXIII-5	(156)
XXX-10	(109)	XXXIII-29	(30)

FIAT Reports

FIAT Number	*List Number*	*FIAT Number*	*List Number*	*FIAT Number*	*List Number*
90	(85)	422	(55)	880	(125)
213	(62)	425	(93)	925	(50)
239	(132)	426	(86)	1,000	(160)
276	(52)	513	(119)	1,305	(158)
362	(100)	806	(22)	1,660	(122)

NTME (USNTME) Reports

NTME Number	*List Number*	*NTME Number*	*List Number*
80-45	(20)	146-45, A.VI	(144)
87-45	(106)	146-45, A.VIII	(145)
111-45	(127)	146-45, A.XV	(146)
144-45	(139)	146-45, A.XVI	(147)
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146-45, A.III	(141)	146-45, A.XVIII	(149)
146-45, A.IV	(142)	187-45	(33)
146-45, A.V	(143)		

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TAC Reports

TAC Number	*List Number*	*TAC Number*	*List Number*	*TAC Number*	*List Number*
AlMl-1	(155)	SnMc-4	(68)	SnMc-10	(70)
SnMc-1	(26)	SnMc-5	(84)	SnMc-11	(69)
SnMc-3	(63)	SnMc-7	(28)	ZGC-2	(108)

TIIC Solid Fuels Sub-committee Reports

TIIC Number	*List Number*	*TIIC Number*	*List Number*
29	(38)	49	(119)

TOM Reports

TOM Number	*List Number*	*TOM Number*	*List Number*	*TOM Number*	*List Number*
5	(26)	9	(63)	17	(108)
6	(155)	10	(68)	22	(132)
8	(25)	11	(84)	41	(69)

Appendix III

SUPPLEMENTAL BIBLIOGRAPHY OF RECENT REFERENCES

ALTHOUGH nearly 400 different references are included in the various chapter bibliographies and are cited in the text the literature on the Fischer-Tropsch process is considerably more voluminous, and many important references were not included for various reasons. To remedy this, the following supplemental bibliography of recent references (1940-1946) has been prepared and divided according to the four sections of the book. No attempt at completeness was attempted even here, incidentally, since only those references are included which seem necessary to round out the coverage of the subjects; little attention, for example, was given to news items and to general reviews on synthetic fuels.

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